Supporting Information

A Selective Approach to Pyridine Appended 1,2,3-Triazolium Salts

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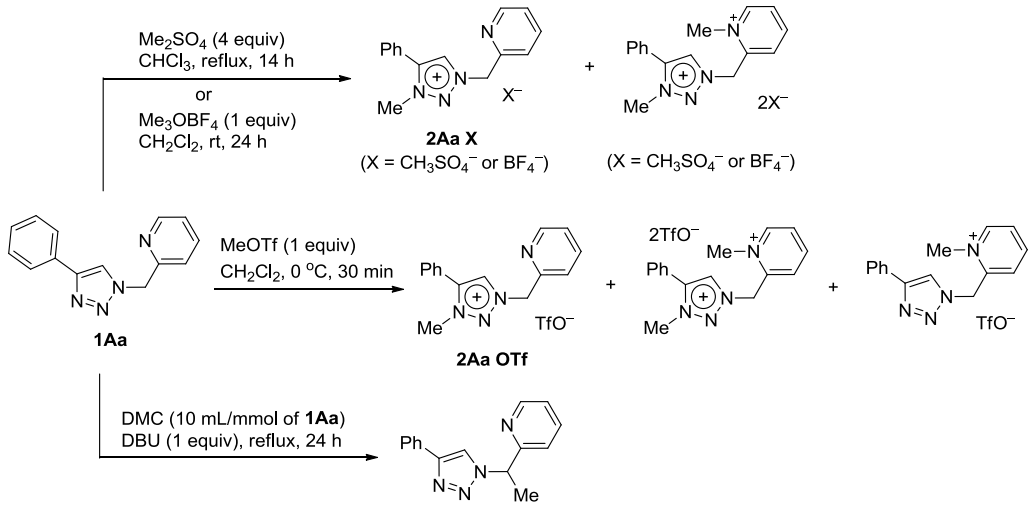
Literature survey

Publications on 1,3,4-trisubstituted-1,2,3-triazolium salts used in the preparation of transition-metal–*tz*NHC complexes and their catalytic properties.[1]

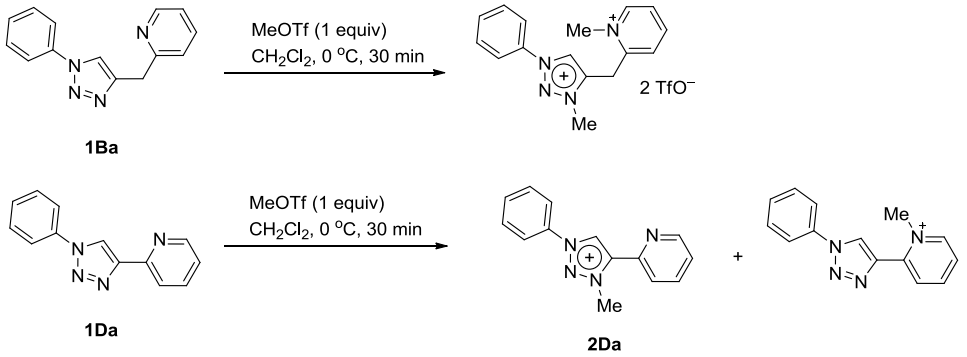
Schemes

Scheme S1. Reactivity of **1Aa** towards methylating reagents.

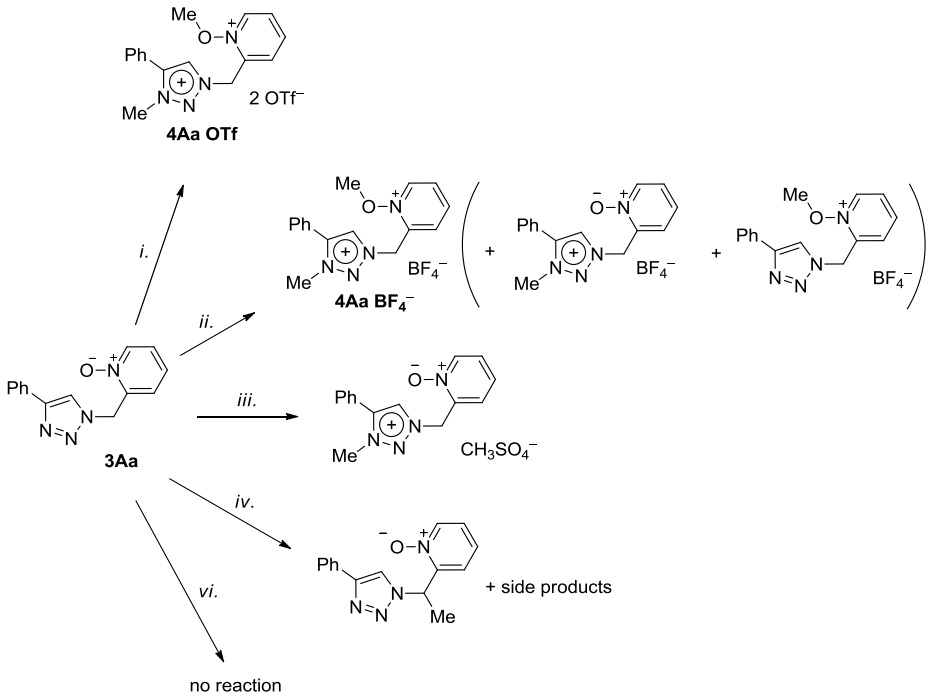


(1) (a) Klein, J. E. M. N.; Holzwarth, M. S.; Hohloch, S.; Sarkar, B.; Plietker B. *Eur. J. Org. Chem.* DOI: 10.1002/ejoc.201300902. (b) Canseco-Gonzalez, D.; Petronilho, A.; Mueller-Bunz, H.; Ohmatsu, K.; Ooi, T.; Albrecht, M. *J. Am. Chem. Soc.* doi.org/10.1021/ja406999p. (c) Hohloch, S.; Scheiffele, D.; Sarkar, B. *Eur. J. Inorg. Chem.* **2013**, 3956–3965. (d) Canseco-Gonzalez, D.; Albrecht, M. *Dalton Trans.* **2013**, *42*, 7424–7432. (e) Ogata, K.; Inomata, S.; Fukuzawa, S. I. *Dalton Trans.* **2013**, *42*, 2362–2365. (f) Hohloch, S.; Frey, W.; Suc, C.-Y.; Sarkar, B. *Dalton Trans.* **2013**, *42*, 11355–11358. (g) Hohloch, S.; Sarkar, B.; Nauton, L.; Cisnetti, F.; Gautier, A. *Tetrahedron Lett.* **2013**, *54*, 1808–1812. (h) Basha Shaik, J.; Ramkumar, V.; Varghese, B.; Sankararaman, S. *Beilstein J. Org. Chem.* **2013**, *9*, 698–704. (i) Saravanakumar, R.; Ramkumar, V.; Sankararaman, S. *J. Organomet. Chem.* **2013**, *736*, 36–41. (j) Nomura, R.; Tsuchiya, Y.; Ishikawa, H.; Okamoto, S. *Tetrahedron Lett.* **2013**, *54*, 1360–1363. (k) Inomata, H.; Ogata, K.; Fukuzawa, S.-i.; Hou, Z. *Org. Lett.* **2012**, *14*, 3986–3989. (l) Zamora, M. T.; Ferguson, M. J.; Cowie, M. *Organometallics* **2012**, *31*, 5384−5395. (m) Keske, E. C.; Zenkina, O. V.; Wang, R.; Crudden, C. M. *Organometallics* **2012**, *31*, 456−461. (n) Keske, E. C.; Zenkina, O. V.; Wang, R.; Crudden, C. M. *Organometallics* **2012**, *31*, 6215−6221. (o) Terashima, T.; Inomata, S.; Ogata, K.; Fukuzawa, S.-i. *Eur. J. Inorg. Chem.* **2012**, *9*, 1387–1393. (p) Guisado-Barrios, G.; Bouffard, J.; Donnadieu, B.; Bertrand, G. *Organometallics* **2011**, *30*, 6017–6021 (q) Nakamura, T.; Terashima, T.; Ogata, K.; Fukuzawa, S.-i. *Org. Lett.* **2011**, *13*, 620–623. (r) Poulain, A.; Canseco-Gonzalez, D.; Hynes-Roche, R.; Müller-Bunz, H.; Schuster, O.; Stoeckli-Evans, H.; Neels, A.; Albrecht, M. *Organometallics* **2011**, *30*, 1021–1029. (s) Cai, J.; Yang, X.; Arumugam, K.; Bielawski, C. W.; Sessler, J. L. *Organometallics* **2011**, *30*, 5033−5037. (t) Saravanakumar, R.; Ramkumar, V.; Sankararaman, S. *Organometallics*, **2011**, *30*, 1689−1694. (u) Prades, A.; Peris, E.; Albrecht, M. *Organometallics*, **2011**, *30*, 1162−1167. (v) Kilpin, K. J.; Paul, U. S. D.; Lee, A.-L.; Crowley, J. D. *Chem. Commun.* **2011**, *47*, 328−330. (w) Aizpurua, J. M.; Sagartzazu-Aizpurua, M.; Azcune, I.; Miranda, J. I.; Monasterio, Z.; García-Lecina, E.; Fratila, R. M. *Synthesis* **2011**, 2737–2742. (x) Inomata, S.; Hiroki, H.; Terashima, T.; Ogata, K.; Fukuzawa, S.-i. *Tetrahedron* **2011**, *67*, 7263–7267. (y) Lalrempuia, R.; McDaniel, N. D.; Müller-Bunz, H.; Bernhard, S.; Albrecht, M. *Angew. Chem. Int. Ed.* **2010**, *122*, 9959–9962. (z) Lalrempuia, R.; McDaniel, N. D.; Müller-Bunz, H.; Bernhard, S.; Albrecht, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 9765–9768.

Scheme S2. Reactivity of **1Ba** and **1Da** towards MeOTf.



Scheme S3. Reactivity of **3Aa** towards methylating reagents.



i.: MeOTf (1 equiv), CH_2Cl_2, 0 °C, 30 min. *ii.*: Me_3OBF_4 (1 equiv), CH_2Cl_2, rt, 24 h. *iii.*: Me_2SO_4 (10 equiv), $CHCl_3$, reflux, 3.5 h. *iv.*: DMC (10 mL/mmol of **3Aa**), DBU (1 equiv), reflux, 24 h. *v.*: MeI (4 equiv), $CHCl_3$, rt, 35 h.

Experimental details

General considerations

The reagents and solvents were used as obtained from the commercial sources (Sigma-Aldrich, Fluka, Alfa Aesar). Pyridyl-triazoles **1A**–**D** (Figure 2) used for this investigation were prepared by copper-catalyzed cycloaddition between the appropriate click partners. For methylation reactions dry glassware and solvents were used. Dichloromethane was dried over 4Å molecular sieves.

NMR spectra were measured on a Bruker Avance 300 and Bruker Avance III 500 spectrometers, using $Si(CH_3)_4$ as internal standard. Proton and carbon spectra were referenced to TMS as the internal standard. Some ^{13}C chemical shifts were determined relative to the ^{13}C signal of the solvent: $CDCl_3$ (77.0 ppm), DMSO-d_6 (39.5 ppm). ^{19}F NMR, ^{11}B NMR and ^{31}P NMR spectra were referenced to CCl_3F, 15% BF_3 etherate in $CDCl_3$ and 85% phosphoric acid, respectively, as external standards at $\delta = 0$. Chemical shifts are given on the δ scale (ppm). Coupling constants (J) are given in Hz. The multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broadened).

Assignments of proton, carbon and nitrogen resonances were performed by standard 2D NMR techniques (^1H-^1H COSY, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC). The numbering used for the assignment of NMR signals is as follows: 1,2,3-triazole ring, simple figures; pyridine ring, primed figures; phenyl ring, double-primed figures (C-1" is attached to the 1,2,3-triazole ring).

An Agilent 6224 time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an Agilent 1260 HLPC was used for recording HRMS spectra.

Elemental analysis was performed with a Perkin-Elmer 2400 Series II CHNS/O Analyzer. IR spectra were obtained with a Perkin–Elmer Spectrum 100, equipped with a Specac Golden Gate Diamond ATR as a solid sample support. Melting points were determined on a Kofler micro hot stage and are uncorrected. The reactions were monitored by TLC on TLC-CARDS SILICA GEL, 220–440 mesh.

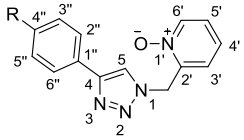
Preparation of triazole appended pyridine *N*-oxides 3A, 3B and 3D

General procedure for the synthesis of pyridine *N*-oxides 3A, 3B and 3D (Figure 3)

A mixture of triazole **1A**, **1B** or **1D** and *m*-CPBA in $CHCl_3$ was refluxed for 30 min. Aqueous solution of $Na_2S_2O_3$ (0.5 M) was added and product was extracted with CH_2Cl_2. Combined organic layers were washed with aqueous NaOH (1 M) and extracted with CH_2Cl_2 to obtain pure pyridine *N*-oxide **3A**, **3B** or **3D**, which were used for further transformations.

For analyses the products were recrystallized from a mixture of EtOH and water. For quantities used in the above procedure, analytical and spectral data of **3A**, **3B** and **3D**, see below.

2-((4-(Aryl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine-*N*-oxides (3A):



3A

2-((4-(Phenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine-*N*-oxide (3Aa, R = H): Compound **1Aa** (237.0 mg, 1.00 mmol), $CHCl_3$ (15 mL), m-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (240.5 mg, 95%). R_f (EtOAc) = 0.1. Mp 129–131 °C. IR: 3238, 1651, 1483, 1209, 1031, 770, 696 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.88 (s, 2H, CH_2), 7.35–7.27 (m, 4H, H-3', H-4', H-5', H-4"), 7.42 (t, *J* = 7.6 Hz, 2H, H-3", H-5"), 7.85 (d, *J* = 6.9 Hz, 2H, H-2", H-6"), 8.23 (s, 1H, H-5), 8.30 (dd, *J* = 6.2, 1.4 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 48.6 (CH_2), 121.6 (C-5), 125.8 (C-2", C-6"), 126.1 (C-4'), 126.1 (C-5'), 126.3 (C-3'), 128.3 (C-4"), 128.8 (C-3", C-5"), 130.3 (C-1"), 139.5 (C-6'), 145.4 (C-2'), 148.1 (C-4). HRMS (ESI+): calcd for $C_{14}H_{12}N_4O^+$ $[M + H]^+$ 253.1011, found 253.1133. Anal. calcd for $C_{14}H_{11}N_4O$: C 66.65, H 4.79, N 22.21; found: C 66.39, H 4.84, N 22.14.

2-((4-(*p*-Tolyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine-*N*-oxide (3Ab, R = Me): Compound **1Ab** (250.0 mg, 1.00 mmol), $CHCl_3$ (15mL), *m*-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (265.0 mg, 99%). R_f (EtOAc) = 0.1. Mp 124–125.0 °C. IR: 3134, 3069, 2921, 1656, 1614, 1495, 1264, 1246, 1044, 856, 801, 767, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.38 (s, 3H, CH_3), 5.86 (s, 2H,

CH_2), 7.31–7.22 (m, 5H, H-3", H-5", H-3', H-4', H-5'), 7.74 (d, *J* = 8.1 Hz, 2H, H-2", H-6"), 8.16 (s, 1H, H-5), 8.30 (dd, *J* = 6.3, 1.4 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.3 (CH_3), 48.5 (CH_2), 121.2 (C-5), 125.7 (C-2", C-6"), 126.0 (C-3'), 126.0 (C-5'), 126.2 (C-4'), 127.5 (C-1"), 129.5 (C-3", C-5"), 138.1 (C-4"), 139.5 (C-6'), 145.5 (C-2'), 148.2 (C-4). HRMS (ESI+): calcd for $C_{15}H_{15}N_4O^+$ $(M+H)^+$ 267.1240, found 267.1241. Anal. calcd for $C_{15}H_{14}N_4O$: C 67.65, H 5.30, N 21.04; found: C 67.50, H 4.98, N 20.76.

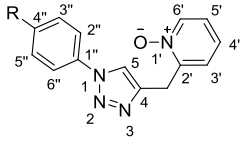
2-((4-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine-*N*-oxide (3Ac, R = OMe): Compound **1Ac** (267.0 mg, 1.00 mmol), $CHCl_3$ (15 mL), *m*-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (249.0 mg, 88%). R_f (EtOAc) = 0.1. Mp 179.0–181 °C. IR: 3137, 3062, 2039, 1935, 1581, 1378, 1030, 810, 789, 675, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.84 (s, 3H, OCH_3), 5.85 (s, 2H, CH_2), 6.95 (d, *J* = 8.8 Hz, 2H, H-3", H-5") 7.33–7.21 (m, 3H, H-3', H-4', H-5'), 7.77 (d, *J* = 8.8 Hz, 2H, H-3", H-5"), 8.12 (s, 1H, H-5), 8.30 (dd, *J* = 6.3, 1.4 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 48.5 (CH_2), 55.3 (OCH_3), 114.2 (C-3", C-5"), 120.7 (C-5), 123.0 (C-1"), 126.0 (C-4'), 126.0 (C-5'), 126.2 (C-3'), 127.1 (C-2", C-6"), 139.5 (C-6'), 145.6 (C-2'), 148.0 (C-4), 159.7 (C-4"). HRMS (ESI+): calcd for $C_{15}H_{15}N_4O_2^+$ $[M + H]^+$ 283.1195, found 283.1190. Anal. calcd for $C_{15}H_{14}N_4O_2$: C 63.82, H 5.00, N 19.85; found: C 63.44, H 5.04, N 19.65.

2-((4-(4-Cyanophenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine-*N*-oxide (3Ad, R = CN): Compound **1Ad** (261.1 mg, 1.00 mmol), $CHCl_3$ (15 mL), *m*-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (257.4 mg, 98%). R_f (EtOAc) = 0.1. Mp 217–219 °C. IR: 3099, 3074, 2964, 2228, 1613, 1438, 1419, 1244, 1221, 1072, 1046, 863, 834, 781, 694 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.86 (s, 2H, CH_2), 7.35–7.27 (m, 2H, H-4', H-5'), 7.43 (dd, *J* = 7.4, 2.4 Hz, 1H, C-3'), 7.71 (d, *J* = 8.4 Hz, 2H, H-3", H-5"), 7.96 (d, *J* = 8.4 Hz, 2H, H-2", H-6"), 8.30 (dd, *J* = 6.2, 1.4 Hz, 1H, H-6'), 8.43 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 48.8 (CH_2), 111.5 (C-4"), 118.8 (CN), 123.1 (C-5), 126.1 (C-2", C-6"), 126.2 (C-5'), 126.5 (C-4'), 126.8 (C-3'), 132.7 (C-3", C-5"), 134.8 (C-1"), 139.7 (C-6'), 144.8 (C-2'), 146.0 (C-4). HRMS (ESI+): calcd for $C_{15}H_{12}N_5O^+$ $[M + H]^+$ 278.1036, found 278.1033. Anal. calcd for $C_{15}H_{11}N_5O$: C 64.97, H 4.00, N 25.26; found: C 65.20, H 3.81, N 25.17.

2-((4-(4-(Trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine-*N*-oxide (3Ae, R = CF_3): Compound **1Ae** (305.0 mg, 1.00 mmol), $CHCl_3$ (15 mL), *m*-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (295.3 mg, 92%). R_f (EtOAc) = 0.1. Mp 201–203 °C. IR: 3106, 2981, 2947, 1694, 1493, 1459, 1328, 1205, 1101, 1081, 1064, 839, 765 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.87 (s, 2H, CH_2), 7.39–7.30 (m, 3H, H-3', H-4', H-5'), 7.67 (d, *J* = 8.1 Hz, 2H, H-3'', H-5'') 7.96 (d, *J* = 8.0 Hz, 2H, H-2'', H-6''), 8.30 (dd, *J* = 6.1, 1.6 Hz, 1H, H-6'), 8.38 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 48.7 (CH_2), 122.6 (C-5), 124.1 (q, *J* = 273 Hz, CF_3), 125.8 (q, *J* = 4 Hz, C-3'', C-5''), 125.9 (C-2'', C-6''), 126.2 (C-4' or C-5'), 126.4 (C-5' or C-4'), 126.6 (C-3'), 130.0 (q, *J* = 33 Hz, C-4''), 133.8 (C-1''), 139.6 (C-6'), 145.0 (C-2'), 146.6 (C-4). ^{19}F NMR (471 MHz, $CDCl_3$): δ = –63 (s, 3F, CF_3). HRMS (ESI+): calcd for $C_{15}H_{12}F_3N_4O^+$ $[M + H]^+$ 321.0958, found 321.0957. Anal. calcd for $C_{15}H_{11}F_3N_4O$: C 56.25, H 3.46, N 17.49; found: C 56.32, H 3.12, N 17.34.

2-((4-(4-Chlorophenyl)-1*H*-1,2,3-triazol-1-yl)methyl)pyridine-*N*-oxide (3Af, R = Cl): Compound **1Af** (271.5 mg, 1.00 mmol), $CHCl_3$ (15 mL), *m*-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (227.0 mg, 80%). R_f (EtOAc) = 0.1. Mp 148–149 °C. IR: 3123, 3063, 3027, 1484, 1446, 1261, 1250, 1224, 1092, 814, 759, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.86 (s, 2H, CH_2), 7.38–7.27 (m, 3H, H-3', H-4', H-5'), 7.39 (d, *J* = 8.5 Hz, 2H, H-3'', H-5'') 7.77 (d, *J* = 8.5 Hz, 2H, H-2'', H-6''), 8.26 (s, 1H, H-5), 8.31 (dd, *J* = 5.6, 1.4 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 48.6 (CH_2), 121.8 (C-5), 126.2 (C-5'), 126.4 (2C, C-3', C-4'), 127.0 (C-2'', C-6''), 128.9 (C-1''), 129.0 (C-3'', C-5''), 134.0 (C-4''), 139.6 (C-6'), 145.2 (C-2'), 147.0 (C-4). HRMS (ESI+): calcd for $C_{14}H_{12}ClN_4O^+$ $[M + H]^+$ 287.0694, found 287.0694. Anal. calcd for $C_{14}H_{11}ClN_4O$: C 58.65%, H 3.87, N 18.54; found: C 58.48, H 3.65, N 18.80.

2-((1-Aryl-1*H*-1,2,3-triazol-4-yl)methyl)pyridine-*N*-oxides (3B):



3B

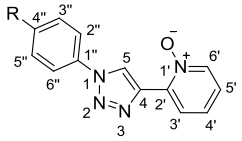
2-((1-Phenyl-1*H*-1,2,3-triazol-4-yl)methyl)pyridine-*N*-oxide (3Ba, R = H): Compound **1Ba** (236.0 mg, 1.00 mmol), $CHCl_3$ (15 mL), *m*-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (252.0 mg, 100%). R_f (EtOAc) = 0.1. Mp 130–131 °C. IR: 3080, 1595, 1493, 1431, 1248, 1227, 1051, 987, 861, 850, 758, 689 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.44 (s, 2H, CH_2), 7.22 (m, 2H, H-4', H-5'), 7.46 (m, 4H, H-3", H-4", H-5", H-3'), 7.73 (d, *J* = 7.6 Hz, 2H, H-2", H-6"), 8.20 (s, 1H, H-5), 8.26 (dd, *J* = 6.5, 1.5 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 27.7 (CH_2), 120.4 (C-2", H-6"), 121.4 (C-5), 124.4 (C-5'), 126.0 (C-4'), 126.5 (C-3'), 128.6 (C-4"), 129.7 (C-3", C-5"), 137.0 (C-1"), 139.4 (C-6'), 143.0 (C-4), 149.1 (C-2'). HRMS (ESI+): calcd for $C_{14}H_{13}N_4O^+$ [M + H]+ 253.1089, found 253.1082. Anal. calcd for $C_{14}H_{12}N_4O$: C 66.65, H 4.79, N 22.21; found: C 66.43, H 4.57, N 22.03.

2-((1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)pyridine-*N*-oxide (3Bc, R = OMe): Compound **1Bc** (266.0 mg, 1.00 mmol), $CHCl_3$ (15 mL), *m*-CPBA (344.0 mg, 2.00 mmol). $Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (267.9 mg, 95%). R_f (EtOAc) = 0.1. Mp 140–142 °C. IR: 3117, 3070, 2932, 1605, 1518, 1492, 1427, 1409, 1388, 1235, 1070, 1070, 1026, 826, 771, 737, 680, 608 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.86 (s, 3H, OCH_3), 4.43 (s, 2H, CH_2), 7.00 (d, *J* = 9.0 Hz, 2H, H-3", H-5"), 7.20 (td, *J* = 7.7, 2.2 Hz, 1H, H-5'), 7.24 (td, *J* = 7.7, 1.5 Hz, 1H, H-4'), 7.46 (dd, *J* = 7.7, 2.2 Hz, 1H, H-3'), 7.85 (d, *J* = 9.0 Hz, 2H, H-2", H-6"), 8.10 (s, 1H, H-5), 8.26 (dd, *J* = 6.4, 1.4 Hz, 1H, H-6'). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 27.7 (CH_2), 55.6 (OCH_3), 114.7 (C-3", C-5"), 121.6 (C-5), 122.2 (C-2", C-6"), 124.3 (C-5'), 125.9 (C-4'), 126.5 (C-3'), 130.6 (C-1"), 139.4 (C-6'), 142.8 (C-4), 149.2 (C-2'), 159.7 (C-4"). HRMS (ESI+): calcd for $C_{15}H_{15}N_4O_2^+$ $[M + H]^+$ 283.1190, found 283.1190. Anal. calcd for $C_{15}H_{14}N_4O_2 \times 1/12H_2O$: C 63.48, H 5.03, N 19.74; found: C 63.47, H 4.87, N 19.38.

2-((1-(4-(Trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)methyl)pyridine-*N*-oxide (3Be, R = CF_3): Compound **1Be** (304.0 mg, 1.00 mmol), $CHCl_3$ (15 mL), *m*-CPBA (344.0 mg, 2.00 mmol).

$Na_2S_2O_3$ (1 × 30 mL), CH_2Cl_2 (2 × 30 mL), NaOH (1 × 60 mL), CH_2Cl_2 (3 × 30 mL). White solid (307.1 mg, 96%). R_f (EtOAc) = 0.1. Mp 141–142 °C. IR: 3138, 3097, 1614, 1433, 1331, 1252, 1160, 1103, 1069, 1050, 1015, 988, 840, 782, 759 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.45 (s, 2H, CH_2), 7.25 (m, 3H, H-4', H-5'), 7.49 (dd, *J* = 7.7, 2.2 Hz, 1H, H-3'), 7.78 (d, *J* = 8.3 Hz, 2H, H-3", H-5"), 7.90 (d, *J* = 8.3 Hz, 2H, H-2", H-6"), 8.26 (dd, *J* = 6.4, 1.5 Hz, 1H, H-6'), 8.31 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 27.9 (CH_2), 120.3 (C-2", C-6"), 121.4 (C-5), 123.5 (q, *J* = 272 Hz, CF_3), 124.6 (C-5'), 126.1 (C-4'), 126.6 (C-3'), 127.1 (q, *J* = 4 Hz, C-3", C-5"), 130.9 (q, *J* = 33 Hz, C-4"), 139.4 (C-1"), 139.5 (C-6'), 143.5 (C-4), 148.8 (C-2'). ^{19}F NMR (471 MHz, $CDCl_3$): δ = –62.6 (s, 3F, CF_3). HRMS (ESI+): calcd for $C_{15}H_{12}F_3N_4O^+$ $[M + H]^+$ 321.0958, found 321.0953. Anal. calcd for $C_{15}H_{11}F_3N_4O \times ¼H_2O$: C 55.47, H 3.57, N 17.25; found: C 55.40, H 3.33, N 17.13.

2-(1-Aryl-1*H*-1,2,3-triazol-4-yl)pyridine-*N*-oxides (3D):



3D

2-(1-phenyl-1*H*-1,2,3-triazol-4-yl)pyridine-*N*-oxide (3Da, R = H): Compound **1Da** (666.0 mg, 3.00 mmol), $CHCl_3$ (50 mL), *m*-CPBA (1.0356 g, 6.00 mmol). $Na_2S_2O_3$ (1 × 90 mL), CH_2Cl_2 (2 × 90 mL), NaOH (1 × 180 mL), CH_2Cl_2 (3 × 90 mL). White solid (644.0 mg, 90%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.7. Mp 180–181 °C. IR: 3210, 3128, 1595, 1501, 1279, 1253, 1027, 840, 757, 705, 685 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.28 (m, 1H, H-5'), 7.44 (ddd, *J* = 8.3, 7.5, 1.2 Hz, 1H, H-4'), 7.49 (m, 1H, H-4"), 7.57 (m, 2H, H-3", H-5"), 7.85 (m, 2H, H-2", H-6"), 8.36 (ddd, *J* = 6.6, 1.2, 0.6 Hz, 1H, H-3'), 8.59 (dd, *J* = 8.1, 2.0 Hz, 1H, H-6'), 9.49 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 120.6 (C-2", C-6"), 124.0 (C-5'), 124.2 (C-5), 124.3 (C-6'), 125.9 (C-4'), 129.0 (C-4"), 129.9 (C-3", C-5"), 136.8 (C-1"), 139.5 (C-4), 140.0 (C-3'), 141.1 (C-2'). HRMS (ESI+): calcd for $C_{13}H_{11}N_4O^+$ $[M + H]^+$ 239.0927, found 239.0926. Anal. calcd for $C_{13}H_{10}N_4O$: C 65.54, H 4.23 , N 23.52; found: C 65.20, H 3.98, N 23.33.

2-(1-(*p*-Tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine-*N*-oxide (3Db, R = Me): Compound **1Db** (708.0 mg, 3.00 mmol), $CHCl_3$ (50 mL), *m*-CPBA (1.036 g, 6.00 mmol). $Na_2S_2O_3$ (1 × 90 mL), CH_2Cl_2 (2 × 90 mL), NaOH (1 × 180 mL), CH_2Cl_2 (3 × 90 mL). White solid (743.4 mg, 98%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.7. Mp 236–238 °C. IR: 3186, 1720, 1517, 1395, 1274, 1215, 1026, 806, 754, 734 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 3H, CH_3), 7.27 (m, 1H, H-

5'), 7.36 (d, *J* = 8.2 Hz, 2H, H-3'', H-5''), 7.43 (td, *J* = 7.9, 1.2 Hz, 1H, H-4'), 7.73 (d, *J* = 8.2 Hz, 2H, H-2'', H-6''), 8.36 (d, *J* = 6.0 Hz, 1H, H-3'), 8.59 (dd, *J* = 8.1, 2.0 Hz, 1H, H-6'), 9.44 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.2 (CH_3), 120.5 (C-2'', C-6''), 123.9 (C-5'), 124.3 (C-5), 124.3 (C-6'), 125.9 (C-4'), 130.4 (C-3'', C-5''), 134.5 (C-1''), 139.2 (C-4''), 139.3 (C-4), 140.0 (C-3'), 141.2 (C-2'). HRMS (ESI+): calcd for $C_{13}H_{10}N_4O^+$ $[M + H]^+$ 239.0927, found 239.0926. Anal. calcd for $C_{13}H_9N_4O \times 1/12H_2O$: C 66.65, H 4.79, N 22.21; found: C 65.96, H 4.58, N 22.16.

2-(1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)pyridine-*N*-oxide (3Dc, R = OMe): Compound **1Dc** (756.0 mg, 3.00 mmol), $CHCl_3$ (50 mL), *m*-CPBA (1.0356 g, 6.00 mmol). $Na_2S_2O_3$ (1 × 90 mL), CH_2Cl_2 (2 × 90 mL), NaOH (1 × 180 mL), CH_2Cl_2 (3 × 90 mL). White solid (752.3 mg, 94%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.7. Mp 164–166 °C. IR: 3217, 2842, 1516, 1468, 1247, 1204, 1029, 825, 767, 635 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.89 (s, 3H, OCH_3), 7.06 (d, *J* = 9.0 Hz, 2H, H-3'', H-5''), 7.27 (m, 1H, H-5'), 7.44 (ddd, *J* = 8.3, 7.6, 1.2 Hz, 1H, H-4'), 7.75 (d, *J* = 9.0 Hz, 2H, H-2'', H-6''), 8.36 (d, *J* = 6.4 Hz, 1H, C-3'), 8.58 (dd, *J* = 8.1, 2.0 Hz, 1H, H-6'), 9.39 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 55.7 (OCH_3), 114.9 (C-2'', C-6''), 122.3 (C-3'', C-5''), 123.9 (C-5'), 124.2 (C-6'), 124.4 (C-5), 126.0 (C-4'), 130.2 (C-1''), 139.3 (C-4), 140.0 (C-3'), 141.3 (C-2'), 160.0 (C-4''). HRMS (ESI+): calcd for $C_{14}H_{13}N_4O_2^+$ $[M + H]^+$ 269.1033, found 269.1031. Anal. calcd for $C_{14}H_{12}N_4O_2$: C 62.68, H 4.51, N 20.88; found: C 62.26, H 4.26, N 20.56.

2-(1-(4-Cyanophenyl)-1*H*-1,2,3-triazol-4-yl)pyridine-*N*-oxide (3Dd, R = CN): Compound **1Dd** (741.0 mg, 3.00 mmol), $CHCl_3$ (50 mL), *m*-CPBA (1.0356 g, 6.00 mmol). $Na_2S_2O_3$ (1 × 90 mL), CH_2Cl_2 (2 × 90 mL), NaOH (1 × 180 mL), CH_2Cl_2 (3 × 90 mL). White solid (676.0 mg, 86%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.7. Mp 276–278 °C. IR: 3180, 2224, 1602, 1514, 1467, 1439, 1396, 1259, 1023, 832, 770 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H, H-5'), 7.97 (td, *J* = 7.7, 1.8 Hz, 1H, H-4'), 8.13 (m, 3H, H-3'', H-5'', H-3'), 8.29 (d, *J* = 8.8 Hz, 2H, H-2'', H-6''), 8.68 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H, H-6'), 9.59 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 112.7 (CN), 117.7 (C-5'), 120.5 (C-5), 120.7 (C-2'', C-6''), 123.8 (C-4''), 124.4 (C-6'), 125.9 (C-4'), 134.0 (C-3'', C-5''), 139.6 (C-1''), 140.0 (C-3'), 140.1 (C-4), 140.6 (C-2'). HRMS (ESI+): calcd for $C_{14}H_{10}N_5O^+$ $[M + H]^+$ 264.0880, found 264.0879. Anal. calcd for $C_{14}H_9N_5O$: C 63.87, H 3.45, N 26.60; found: C 63.91, H 3.21, N 26.59.

2-(1-(4-(Trifluoromethyl)phenyl)-1*H*-1,2,3-triazol-4-yl)pyridine-*N*-oxide (3De, R = CF_3): Compound **1De** (741.0 mg, 3.00 mmol), $CHCl_3$ (50 mL), *m*-CPBA (1.0356 g, 6.00 mmol). $Na_2S_2O_3$ (1 × 90 mL), CH_2Cl_2 (2 × 90 mL), NaOH (1 × 180 mL), CH_2Cl_2 (3 × 90 mL). White solid (830.1 mg, 90%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.7. Mp 213–215 °C. IR: 3187, 1612, 1401, 1320, 1259, 1163, 1099, 1062, 1026, 838, 810, 763 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.29 (ddd, *J* = 7.5, 6.6, 2.1 Hz, 1H, H-5'), 7.46 (td, *J* = 7.9, 1.2 Hz, 1H, H-4'), 7.85 (d, *J* = 8.3 Hz, 2H, H-3'', H-5''), 8.02 (d, *J* = 8.3 Hz, 2H, H-2'', H-6''), 8.38 (dd, *J* = 6.5, 1.3 Hz, 1H, H-3'), 8.60 (dd, *J* = 8.1, 2.0 Hz, 1H, H-6'), 9.58 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 120.5 (C-2'', C-6''), 123.6 (q, *J* = 272 Hz, CF_3), 124.0 (C-5), 124.3 (C-5'), 124.4 (C-6'), 126.0 (C4'), 127.3 (q, *J* = 4 Hz, C3'', C5''), 131.0 (q, *J* = 33 Hz, C4''), 139.2 (C1''), 139.9 (C4), 140.0 (C3'), 140.8 (C2'). ^{19}F NMR (471 MHz, $CDCl_3$): δ = –63 (s, 3F, CF_3). HRMS (ESI+): calcd for $C_{14}H_{10}N_4F_3O^+$ $[M + H]^+$ 307.0801, found 307.0799. Anal. calcd for $C_{14}H_9N_4F_3O$: C 54.91, H 2.96, N 18.29; found: C 54.49, H 2.81, N 17.83.

2-(1-(4-Bromophenyl)-1*H*-1,2,3-triazol-4-yl)pyridine-*N*-oxide (3Dg, R = Br): Compound **1Dg** (903.0 mg, 3.00 mmol), $CHCl_3$ (50 mL), *m*-CPBA (1.0356 g, 6.00 mmol). $Na_2S_2O_3$ (1 × 90 mL), CH_2Cl_2 (2 × 90 mL), NaOH (1 × 180 mL), CH_2Cl_2 (3 × 90 mL). White solid (911.8 mg, 96%). R_f (CH_2Cl_2 : MeOH = 10 : 1)= 0.7. Mp 197–199 °C. IR: 3111, 1773, 1563, 1495, 1469, 1394, 1251, 1206, 1009, 986, 950, 815, 722, 678 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 7.8 Hz, 1H, H-5'), 7.45 (ddd, *J* = 8.4, 7.9, 1.2 Hz, 1H, H-4'), 7.70 (d, *J* = 8.9 Hz, 2H, H-3'', H-5''), 7.75 (d, *J* = 8.9 Hz, 2H, H-2'', H-6''), 8.36 (d, *J* = 6.5 Hz, 1H, H-3'), 8.58 (dd, *J* = 8.1, 2.0 Hz, 1H, H-6'), 9.48 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 122.0 (C-2'', C-6''), 122.7 (C-4''), 124.0 (C-5'), 124.2 (C-5), 124.3 (C-6'), 126.0 (C-4'), 133.0 (C-3'', C-5''), 135.8 (C-1''), 139.7 (C-4), 140.0 (C-3'), 140.9 (C-2'). HRMS (ESI+): calcd for $C_{13}H_{10}BrN_4O^+$ $[M + H]^+$ 317.0033, found 317.0030. Anal. calcd for $C_{13}H_9BrN_4O$: C 49.23, H 2.86, N 17.67; found: C 49.34, H 2.84, N 17.91.

Methoxypyridinium-triazolium salts 4A

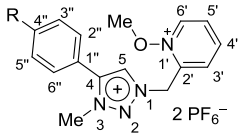
General procedure for dimethylation of triazole appended pyridyl *N*-oxides 3A into 4A (Scheme 4)

Pyridine *N*-oxide **3A** in dry CH_2Cl_2 was purged with dry argon and stirred on an ice-bath at 0 °C for a few minutes. MeOTf was added via syringe and the reaction mixture was stirred at 0 °C for 30 min. The solvent was evaporated to dryness using rotary evaporator affording pure **4A** 2**OTf**, which was used without further manipulations for the reductive N–O cleavage into **2A**.

The yields are given below for the trifluoromethanesulfonates **4A** 2**OTf**.

For all other analyses, crude **4A** 2**OTf** was dissolved in MeOH. After addition of NH_4PF_6 the precipitated **4A 2PF$_6$** was collected by filtration and thoroughly washed with Et_2O. For quantities used in the above procedure, analytical and spectral data of **4A 2PF$_6$**, see below.

Methoxypyridinium-triazolium salts 4A



4A 2PF$_6$

1-Methoxy-2-((3-methyl-4-phenyl-1*H*-1,2,3-triazolium-1-yl)methyl)pyridinium salt (4Aa, R = H): Compound **3Aa** (252 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL).

4Aa 2OTf: conversion 96% based on ^{1}H NMR analysis.

4Aa 2PF$_6$: NH_4PF_6 (652 mg, 4.00 mmol), white solid (398 mg, 70%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.3. Mp 149–151 °C. IR: 3140, 1615, 1584, 1493, 1446, 1278, 1157, 820, 782 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.32 (s, 3H, CH_3-trz), 4.56 (s, 3H, OCH_3-py), 6.55 (s, 2H, CH_2), 7.75–7.69 (m, 5H, H-2", H-3", H-4", H-5", H-6"), 8.40–8.36 (m, 2H, H-3', H-5'), 8.73 (td, *J* = 7.8, 1.3 Hz, 1H, H-4'), 9.30 (s, 1H, H-5), 9.76 (dd, *J* = 6.5, 1.2 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.5 (CH_3-trz), 50.2 (CH_2), 69.6 (OCH_3-py), 122.2 (C-1"), 129.3 (C-3", C-5" or C-2", C-6"), 129.5 (C-2", C-6" or C-3", C-5"), 129.9 (C-5'), 130.0 (C-3'), 130.5 (C-5), 131.7 (C-4"), 141.5 (C-6'), 142.7 (C-4), 145.2 (C-2'), 145.6 (C-4'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.2 (d, *J* = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, *J* = 712 Hz,

1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{18}N_4O^{2+}$ $[M]^{2+}$ 141.0735, found 141.0750. Anal. calcd for $C_{16}H_{18}F_{12}N_4OP_2$: C 33.58, H 3.17, N 9.79; found: C 33.81, H 2.90, N 9.83.

1-Methoxy-2-((4-(*p*-tolyl)-3-methyl-1*H*-1,2,3-triazolium-1-yl)methyl)pyridinium salt (4Ab, R = Me): Compound **3Ab** (275.0 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL).

4Ab 2OTf: conversion 96% based on ^{1}H NMR analysis.

4Ab 2PF$_6$: NH_4PF_6 (652 mg, 4.00 mmol), wite solid (385.0 mg, 70%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.3. Mp 155–157 °C. IR: 3144, 1616, 1590, 1505, 1279, 825, 726, 714 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.44 (s, 3H, CH_3), 4.31 (s, 3H, CH_3-trz), 4.55 (s, 3H, OCH_3-py), 6.53 (s, 2H, CH_2), 7.51 (d, *J* = 7.9 Hz, 2H, H-3", H-5"), 7.64 (d, *J* = 8.3 Hz, 2H, H-2", H-6"), 8.36 (dd, *J* = 8.0, 1.8 Hz, 1H, H-3'), 8.39 (ddd, *J* = 8.0, 6.6, 1.8 Hz, 1H, H-5'), 8.72 (td, *J* = 7.9, 1.2 Hz, 1H, H-4'), 9.26 (s, 1H, H-5), 9.75 (dd, *J* = 6.6, 1.3 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 21.0 (CH_3), 39.0 (CH_3-trz), 50.2 (CH_2), 69.6 (OCH_3-py), 119.3 (C-1"), 129.2 (C-2", C-6"), 129.9 (C-3'), 130.0 (C-5'), 130.0 (C-3", C-5"), 130.2 (C-5), 141.5 (C-6'), 141.9 (C-4"), 142.8 (C-4), 145.2 (C-2'), 145.6 (C-4'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.2 (d, *J* = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, *J* = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{17}H_{20}N_4O^{2+}$ $[M]^{2+}$ 148.0813, found 148.0820. Anal. calcd for $C_{17}H_{20}F_{12}N_4OP_2$: C 34.83, H 3.44, N 9.56; found: C 35.03, H 3.14, N 9.51.

1-Methoxy-2-((4-(4-methoxyphenyl)-3-methyl-1*H*-1,2,3-triazolium-1-yl)methyl)pyridinium salt (4Ac, R = OMe): Compound **3Ac** (282 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL).

4Ac 2OTf: conversion 94% based on ^{1}H NMR analysis.

4Ac 2PF$_6$: NH_4PF_6 (652 mg, 4.00 mmol), white solid (453 mg, 80%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.3. Mp 147–149 °C. IR: 3141, 3117, 1614, 1509, 1266, 1183, 822, 723 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.87 (s, 3H, OCH_3), 4.29 (s, 3H, CH_3-Ntrz), 4.55 (s, 3H, OCH_3-py), 6.52 (s, 2H, CH_2), 7.24 (d, *J* = 8.9 Hz, 2H, H-2", H-6"), 7.69 (d, *J* = 8.8 Hz, 2H, H-3", H-5"), 8.35 (dd, *J* = 7.9, 1.8 Hz, 1H, H-3'), 8.39 (ddd, *J* = 8.1, 6.6, 1.8 Hz, 1H, H-5'), 8.72 (td, *J* = 7.8, 1.2 Hz, 1H, H-4'), 9.22 (s, 1H, H-5), 9.75 (dd, *J* = 6.6, 1.2 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.0 (CH_3-trz), 50.2 (CH_2), 55.6 (OCH_3), 69.6 (OCH_3-py), 114.1 (C-1"), 114.9 (C-2", C-6"), 129.9 (C-3'), 129.9 (C-5), 130.0 (C-5'), 131.0 (C-3", C-5"), 141.5 (C-6'), 142.7 (C-4), 145.2 (C-2'), 145.6 (C-4'), 161.7 (C-4"). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.2 (d, *J* = 712 Hz, 6F,

PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, J = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{17}H_{20}N_4O_2^{2+}$ $[M]^{2+}$ 156.0788, found 156.0804. Anal. calcd for $C_{17}H_{20}F_{12}N_4O_2P_2$: C 33.90, H 3.35, N 9.30; found: C 33.98, H 2.91, N 9.27.

2-((4-(4-Cyanophenyl)-3-methyl-1*H*-1,2,3-triazolium-1-yl)methyl)-1-methoxypyridinium salt (4Ad, R = CN): Compound **3Ad** (279.1 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL).

4Ad 2OTf: conversion 93% based on ^1H NMR analysis.

4Ad 2PF$_6$: NH_4PF_6 (652 mg, 4.00 mmol), white solid (450 mg, 76%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.3. Mp 166–168 °C. IR: 3128, 2233, 1616, 1588, 1457, 1277, 1180, 823, 741 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.34 (s, 3H, CH_3-trz), 4.55 (s, 3H, OCH_3-py), 6.57 (s, 2H, CH_2), 7.95 (d, J = Hz, 2H, H-2", H-6"), 8.20 (d, J = Hz, 2H, H-3", H-5"), 8.35 (dd, J = 8.0, 1.8 Hz, 1H, H-3'), 8.40 (ddd, J = 8.0, 6.6, 1.8 Hz, 1H, H-5'), 8.73 (td, J = 7.8, 1.2 Hz, 1H, H-4'), 9.39 (s, 1H, H-5), 9.76 (dd, J = 6.7, 1.2 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.7 (CH_3-trz), 50.3 (CH_2), 69.6 (OCH_3-py), 114.2 (C-4"), 117.9 (CN), 126.7 (C-1"), 129.9 (C-3'), 130.0 (C-5'), 130.4 (C-2", C-6"), 131.3 (C-5), 133.3 (C-3", C-5"), 141.3 (C-4), 141.5 (C-6'), 145.1 (C-2'), 145.6 (C-4'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.2 (d, J = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, J = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{17}H_{17}N_5O^{2+}$ $[M]^{2+}$ = 153.5711, found 153.5711. Anal. calcd for $C_{17}H_{17}F_{12}N_5OP_2$: C 34.19, H 2.87, N 11.73; found: C 34.48, H 2.72, N 11.74.

1-Methoxy-2-((4-(4-(trifluoromethyl)phenyl)-3-methyl-1*H*-1,2,3-triazolium-1-yl)methyl)pyridinium salt (4Ae, R = CF_3): Compound **3Ae** (319.2 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL).

4Ae 2OTf: conversion 92% based on ^1H NMR analysis.

4Ae 2PF$_6$: NH_4PF_6 (652 mg, 4.00 mmol), white solid (480.8 mg, 75%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.3. Mp 161–163 °C. IR: 3151, 1618, 1595, 1505, 1446, 1412, 1357, 1170, 1133, 1117, 1072, 1015, 831, 815, 686, 647 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.34 (s, 3H, CH_3-trz), 4.55 (s, 3H, OCH_3-py), 6.58 (s, 2H, CH_2), 7.98 (d, J = 8.1 Hz, 2H, H-2", H-6"), 8.10 (d, J = 8.1 Hz, 2H, H-3", H-5"), 8.35 (dd, J = 8.0, 1.8 Hz, 1H, H-3'), 8.40 (ddd, J = 8.1, 6.8, 1.8 Hz, 1H, H-5'), 8.73 (td, J = 7.8, 1.2 Hz, 1H, H-4'), 9.38 (s, 1H, H-5), 9.77 (dd, J = 6.7, 1.3 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.0 (CH_3-trz), 50.3 (CH_2), 69.6 (OCH_3-py), 125.3 (q, J = 272 Hz, CF_3), 126.3 (q, J = 4 Hz, C-3", C-5"), 128.4 (q, J = 33 Hz, C-4"), 129.2 (C-1"), 129.8 (C-3'),

130.0 (C-5'), 130.6 (2C, C-2", C-6"), 131.3 (C-5), 141.5 (C-6'), 141.5 (C-4), 145.2 (C-2'), 145.6 (C-4'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –61.6 (s, 3F, CF_3), –70.2 (d, J = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, J = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{17}H_{17}F_3N_4O^{2+}$ $[M]^{2+}$ = 157.0672, found 175.0677. Anal. calcd for $C_{17}H_{17}F_{15}N_4OP_2 \times 5/6$ NH_4PF_6: C 26.21, H 2.72, N 8.99; found: C 26.24, H 2.94, N 9.37.

2-((4-(4-Chlorophenyl)-3-methyl-1*H*-1,2,3-triazolium-1-yl)methyl)-1-methoxypyridinium salt (4Af, R = Cl): Compound **3Af** (285.7 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL).

4Af 2OTf: conversion 94% based on ^{1}H NMR analysis.

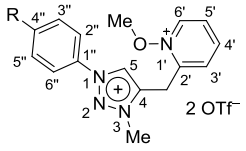
4Af 2PF$_6$: NH_4PF_6 (652 mg, 4.00 mmol), white solid (385.7 mg, 68%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.3. Mp 161.5–163 °C. IR: 3143, 1613, 1486, 1455, 1275, 1158, 818, 720, cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.31 (s, 3H, CH_3-trz), 4.55 (s, 3H, OCH_3-py), 6.55 (s, 2H, CH_2), 7.63–7.93 (m, 4H, H-2", H-3", H-5", H-6"), 8.35 (dd, J = 8.0, 1.8 Hz, 1H, H-3'), 8.40 (ddd, J = 8.0, 6.6, 1.8 Hz, 1H, H-5'), 8.72 (td, J = 7.8, 1.2 Hz, 1H, H-4'), 9.26 (s, 1H, H-5), 9.76 (dd, J = 6.7, 1.2 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.0 (CH_3-trz), 50.3 (CH_2), 69.6 (OCH_3-py), 121.1 (C-1"), 129.6 (C-3", C-5" or C-2", C-6"), 129.8 (C-3'), 130.0 (C-5'), 130.7 (C-5), 131.3 (C-2", C-6" or C-3", C-5"), 136.8 (C-4"), 141.5 (C-6'), 141.8 (C-4), 145.2 (C-2'), 145.6 (C-4'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.2 (d, J = 711.5 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, J = 711.5 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{17}ClN_4O^{2+}$ $[M]^{2+}$ 158.0540, found 158.0547. Anal. calcd for $C_{16}H_{17}ClF_{12}N_4OP_2$: C 31.67, H 2.82, N 9.23; found: C 31.75, H 2.54, N 9.16.

Methoxypyridinium-triazolium salts 4B

General procedure for dimethylation of triazole appended pyridyl *N*-oxides 3B into 4B (Scheme 4)

Pyridine *N*-oxide **3B** in dry CH_2Cl_2 was purged with dry argon and stirred on an ice-bath at 0 °C for a few minutes. MeOTf was added via syringe and the reaction mixture was stirred at 0 °C for 30 min. The solvent was evaporated to dryness using rotary evaporator affording pure **4B 2OTf**, which was used without further manipulations for the reductive N–O cleavage into **2B**.

Methoxypyridinium-triazolium salts 4B



4B 2OTf

1-Methoxy-2-((3-methyl-1-phenyl-1*H*-1,2,3-triazolium-4-yl)methyl)pyridinium trifluoromethanesulphonate (4Ba 2OTf, R = H): Compound **3Ba** (252.0 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL). White solid (481.4 mg, 83%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.4. Mp 130–132 °C. IR: 3093, 1585, 1503, 1447, 1255, 1153, 1029, 957, 919, 785, 764, 634 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.43 (s, 3H, CH_3-trz), 4.52 (s, 3H, OCH_3-py), 5.04 (s, 2H, CH_2), 7.83–7.71 (m, 3H, H-3", H-4", H-5"), 7.96 (dd, *J* = 7.9, 1.9 Hz, 2H, H-2", H-6"), 8.32 (dd, *J* = 7.8, 6.4 Hz, 2H, H-3', H-5'), 8.65 (td, *J* = 7.9, 1.2 Hz, 1H, H-4'), 9.49 (s, 1H, H-5), 9.67 (d, *J* = 6.0 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 24.6 (CH_2), 38.5 (CH_3-trz), 69.3 (OCH_3-py), 121.4 (C-2", C-6"), 128.8 (C-5', C-5), 130.1 (C-3'), 130.5 (2C, C-3", C-5"), 131.9 (C-4"), 134.6 (C-1"), 138.3 (C-4), 141.4 (C-6'), 145.3 (C-4'), 147.5 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{16}H_{18}N_4O^{2+}$ $[M]^{2+}$ 141.0735, found 141.0750. Anal. calcd for $C_{18}H_{18}F_6N_4O_7S_2$: C 37.24, H 3.13, N 9.65; found: C 37.54, H 2.95, N 9.73.

1-Methoxy-2-((1-(4-methoxyphenyl)-3-methyl-1*H*-1,2,3-triazolium-4-yl)methyl)pyridinium trifluoromethanesulphonate (4Bc 2OTf, R = OMe): Compound **3Bc** (282.0 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.50 mmol, 0.5 mL). White solid (372.1 mg, 61%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.4. Mp 103–104 °C. IR: 3042, 1582, 1514, 1252, 1225, 1165, 1144, 1027, 843, 787, 635 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 3.88 (s, 3H, OCH_3), 4.40 (s, 3H, CH_3-trz), 4.51 (s, 3H, OCH_3-py), 5.02 (s, 2H, CH_2), 7.28 (d, *J* = 9.0 Hz, 2H, H-3", H-5"), 7.89 (d, *J* = 9.0 Hz, 2H, H-2", H-6"), 8.32 (d, *J* = 7.9 Hz, 2H, H-3', H-5'), 8.65 (t, *J* = 7.8 Hz, 1H, H-4'), 9.39 (s, 1H, H-5), 9.67 (d, *J* = 6.5 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 24.6 (CH_2), 38.3 (CH_3-trz), 55.9 (OCH_3), 69.3 (OCH_3-py), 115.4 (C-3", C-5"), 123.0 (C-2", C-6"), 127.6 (C-1"), 128.4 (C-5), 128.8 (C-5' or C-3'), 130.1 (C-3' or C-5'), 138.1 (C-4), 141.4 (C-6'), 145.3 (C-4'), 147.5 (C-2'), 161.5 (C-4"). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{17}H_{20}N_4O_2^{2+}$ $[M]^{2+}$ 156.0788, found 156.0789. Anal. calcd for $C_{19}H_{20}F_6N_4O_8S_2$: C 37.38, H 3.30, N 9.18; found: C 37.08, H 3.20, N 9.03.

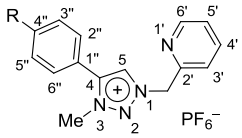
1-Methoxy-2-((3-methyl-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazolium-4-yl)methyl)pyridinium trifluoromethanesulphonate (4Be 2OTf, R = CF_3): Compound **3Be** (320.0 mg, 1.0 mmol), CH_2Cl_2 (5 mL), MeOTf (750 mg, 4.5 mmol, 0.5 mL). White solid (505.4 mg, 78%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.4. Mp 160–161 °C. IR: 3083, 1616, 1322, 1259, 1225, 1137, 1066, 1028, 989, 959, 851, 838, 789, 689, 635 cm^{-1}. ^1H NMR (DMSO-d_6): δ = 4.47 (s, 3H, CH_3-trz), 4.52 (s, 3H, OCH_3-py), 5.07 (s, 2H, CH_2), 8.21 (d, 4H, *J* = 4.4 Hz, H-2", H-3", H-5", H-6"), 8.35–8.31 (m, 2H, H-3', H5'), 8.66 (td, *J* = 7.8, 1.2 Hz, 1H, H-4'), 9.60 (s, 1H, H-5), 9.68 (d, *J* = 5.9 Hz 1H, H-6'). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 24.6 (CH_2), 38.7 (CH_3-trz), 69.3 (OCH_3-py), 122.4 (C-2", C-6"), 123.5 (q, *J* = 273 Hz, CF_3), 127.8 (q, *J* = 4 Hz, C-3", C-5"), 128.8 (C-5'), 129.3 (C-5), 130.1 (C-3'), 131.7 (q, *J* = 6 Hz, C-4"), 137.4 (C-1"), 138.5 (C-4), 141.4 (C-6'), 145.3 (C-4'), 147.4 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –61.4 (CF_3), –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{17}H_{17}F_3N_4O^{2+}$ [M] $^{2+}$ 175.0672, found 175.0673. Anal. calcd for $C_{19}H_{17}F_9N_4O_7S_2$: C 35.19, H 2.64, N 8.64; found: C 35.50, H 2.60, N 8.76.

Reductive cleavage of N–O bond in 4A 2OTf and 4B 2OTf into pyridy-triazolium salts 2A PF_6 and 2B PF_6 (Scheme 5)

General procedure

A stirred solution of **4A 2OTf** or **4B 2OTf** and $Mo(CO)_6$ in abs. EtOH was heated under reflux for 1 h. The reaction mixture was concentrated using rotary evaporator and subjected to column chromatography (CH_2Cl_2 : MeOH = 5 : 1, R_f ≈ 0.5). Product (**2A 2OTf** or **2B 2OTf**) was dissolved in water and KPF_6 (2 equiv) was added. After cooling the precipitated pure **2A PF_6** or **2B PF_6** was collected by filtration. For quantities used in the above procedure, analytical and spectral data of **2A PF_6** and **2B PF_6**, see below.

1-(Pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium salts 2A



2A PF_6

3-Methyl-4-phenyl-1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Aa PF_6, R = H): Compound **4Aa 2OTf** (580.3 mg, 1.00 mmol), EtOH (10 mL), $Mo(CO)_6$ (528 mg, 2.00 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (388.3 mg, 98%).

R_f (CH_2Cl_2 : MeOH=5:1) = 0.5. Mp 128–129 °C. IR: 3151, 3135, 1591, 1573, 1441, 1211, 1155, 1079, 1019, 998, 828, 768, 756, 699 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.32 (s, 3H, CH_3-trz), 6.08 (s, 2H, CH_2), 7.47 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H, H-5'), 7.67 (m, 4H, H-3', H-3", H-4", H-5"), 7.77 (d, *J* = 7.8 Hz, 2H, H-2", H-6"), 7.95 (dt, *J* = 7.7, 1.8 Hz, 1H, H-4'), 8.60 (dd, *J* = 3.1, 1.7 Hz, 1H, H-6'), 9.30 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.4 (CH_3-trz), 57.2 (CH_2), 122.5 (C-1"), 123.3 (C-3'), 124.2 (C-5'), 129.3 (C-2", C-6"), 129.4 (C-3", C-5"), 129.7 (C-5), 131.5 (C-4"), 137.7 (C-4'), 142.5 (C-4), 149.7 (C-6'), 151.9 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.1 (d, *J* = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –144 (septet, *J* = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{15}H_{15}N_4^+$ $[M]^+$ = 251.1291, found 251.1286. Anal. calcd for $C_{15}H_{15}F_6N_4P \times 1/3\ H_2O$: C 44.79, H 3.93, N 13.93; found: C 44.80, H 3.74, N 13.73.

3-Methyl-1-(pyridin-2-ylmethyl)-4-(p-tolyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Ab PF_6, R = Me): Compound **4Ab 2OTf** (596.1 mg, 1.00 mmol), EtOH (10 mL), $Mo(CO)_6$ (528 mg, 2.00 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (266.7 mg, 93%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.5. Mp 111–112 °C. IR: 3152, 1621, 1595, 1574, 1511, 1474, 1408, 1376, 1344, 1194, 1162, 829, 759 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.42 (s, 3H, CH_3), 4.30 (s, 3H, CH_3-trz), 6.06 (s, 2H, CH_2), 7.48 (d, *J* = 8.5 Hz, 3H, H-5', H-3", H-5"), 7.66 (d, *J* = 8.2 Hz, 3H, H-3', H-2", H-6"), 7.95 (td, *J* = 7.7, 1.8 Hz, 1H, H-4'), 8.59 (dt, *J* = 5.4, 1.3 Hz, 1H, H-6'), 9.26 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 21.0 (CH_3), 39.5 (CH_3-trz), 57.2 (CH_2), 119.6 (C-1"), 123.2 (C-3'), 124.1 (C-5'), 129.2 (C-2", C-6"), 129.4 (C-5), 129.9 (C-3", C-5"), 137.7 (C-4'), 141.6 (C-4"), 142.5 (C-4), 149.7 (C-6'), 151.9 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.1 (d, *J* = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –144 (septet, *J* = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{17}N_4^+$ $[M]^+$ = 265.1448, found 265.1450. Anal. calcd for $C_{16}H_{17}F_6N_4P$: C 46.84, H 4.18, N 13.66; found: C 46.60, H 3.99, N 13.47.

4-(4-Methoxyphenyl)-3-methyl-1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Ac PF_6, R = OMe): Compound **4Ac 2OTf** (610 mg, 1.00 mmol), EtOH (10 mL), $Mo(CO)_6$ (528 mg, 2.00 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (413 mg, 97%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.5. Mp 105–108 °C. IR: 3152, 2843, 1618, 1596, 1574, 1509, 1440, 1260, 829, 755 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 3.87 (s, 3H, OCH_3), 4.29 (s, 3H, CH_3-trz), 6.08 (s, 2H, CH_2), 7.21 (d, *J* = 8.9 Hz, 2H, H-3", H-5"),

7.46 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H, H-5'), 7.65 (d, *J* = 7.8 Hz, 1H, H-3'), 7.71 (d, *J* = 8.8 Hz, 2H, H-2'', H-6''), 7.95 (td, *J* = 7.7, 1.8 Hz, 1H, H-4'), 8.59 (dt, *J* = 4.9, 1.3 Hz, 1H, H-6'), 9.22 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.4 (CH_3-trz), 55.5 (OCH_3), 57.2 (CH_2), 114.5 (C-1''), 114.8 (C-3'', C-5''), 123.2 (C-3'), 124.1 (C-5'), 129.1 (C-5), 131.0 (C-2'', C-6''), 137.7 (C-4'), 142.4 (C-4), 149.7 (C-6'), 152.0 (C-2'), 161.5 (C-4''). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.1 (d, *J* = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –144 (septet, *J* = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{17}N_4O^+$ $[M]^+$ = 281.1397, found 281.1399. Anal. calcd for $C_{16}H_{17}F_6N_4OP \times 1/2H_2O$: C 44.15, H 4.17, N 12.87; found: C 43.85, H 3.82, N 12.69.

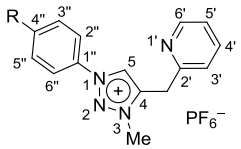
4-(4-Cyanophenyl)-3-methyl-1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Ad PF_6, R = CN): Compound **4Ad 2OTf** (582.0 mg, 1.00 mmol), EtOH (10 mL), $Mo(CO)_6$ (528 mg, 2.00 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (315.2 mg, 99%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.5. Mp 93–95 °C. IR: 3152, 2232, 1598, 1576, 1405, 1344, 1318, 1195, 1162, 1079, 1015, 997, 826, 760 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.34 (s, 3H, CH_3-trz), 6.11 (s, 2H, CH_2), 7.47 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1H, H-5'), 7.66 (d, *J* = 7.9 Hz, 1H, H-3'), 7.96 (dd, *J* = 7.7, 1.8 Hz, 1H, H-4'), 7.97 (d, *J* = 8.3 Hz, 2H, H-2'', H-6''), 8.17 (d, *J* = 8.4 Hz, 2H, H-3'', H-5'') 8.60 (d, *J* = 4.7 Hz, 1H, H-6'), 9.39 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.2 (CH_3-trz), 57.3 (CH_2), 114.0 (C-4''), 118.0 (CN), 123.3 (C-3'), 124.2 (C-5'), 127.1 (C-1''), 130.4 (C-2'', C-6''), 130.5 (C-5), 133.1 (C-3'', C-5''), 137.7 (C-4'), 141.0 (C-4), 149.8 (C-6'), 151.8 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.1 (d, *J* = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –144 (septet, *J* = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{14}N_5^+$ $[M]^+$ = 276.1244, found 276.1242. Anal. calcd for $C_{16}H_{14}F_6N_5P$: C 45.62, H 3.35, N 16.62; found: C 45.69, H 3.19, N 16.19.

3-Methyl-1-(pyridin-2-ylmethyl)-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Ae PF_6, R = CF_3): Compound **4Ae 2OTf** (648.1 mg, 1.00 mmol), EtOH (10 mL), $Mo(CO)_6$ (528 mg, 2.00 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (323.1 mg, 94%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.5. Mp 118–120 °C. IR: 3147, 1595, 1576, 1442, 1410, 1376, 1195, 1129, 1110, 1073, 1035, 1016, 830, 762 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.34 (s, 3H, CH_3-trz), 6.11 (s, 2H, CH_2), 7.47 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H, H-5'), 7.67 (d, *J* = 7.8 Hz, 1H, H-3'), 7.96 (td, *J* = 7.7, 1.8 Hz, 1H, H-4'), 8.00 (d, *J* = 8.1 Hz, 2H, H-2'', H-6''), 8.06 (d, *J* = 8.2 Hz, 2H, H-3'', H-5'') 8.60 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H, H-6'), 9.39 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 38.9 (CH_3-trz), 57.3 (CH_2), 123.3

(C-3'), 123.7 (q, J = 273 Hz, CF_3), 124.2 (C-5'), 126.2 (q, J = 4 Hz, C-3", C-5"), 126.7 (C-1"), 130.4 (C-5), 130.5 (C-2", C-6"), 131.3 (q, J = 33 Hz, C-4"), 137.7 (C-4'), 141.2 (C-4), 149.8 (C-6'), 151.9 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –61.5 (s, 3F, CF_3), –70.1 (d, J = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –144 (septet, J = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{14}F_3N_4^+$ $[M]^+$ = 319.1165, found 319.1164. Anal. calcd for $C_{16}H_{14}F_9N_4P$: C 41.39, H 3.04, N 12.07; found: C 41.72, H 2.83, N 12.07.

4-(4-Chlorophenyl)-3-methyl-1-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Af PF_6, R = Cl): Compound **4Af 2OTf** (617.0 mg, 1.00 mmol), EtOH (10 mL), $Mo(CO)_6$ (528 mg, 2.000 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (206.3 mg, 92%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.5. Mp 113–115 °C. IR: 3160, 1615, 1599, 1577, 1489, 1476, 1442, 1257, 1195, 1091, 1012, 830, 761, 741, 725 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.31 (s, 3H, CH_3-trz), 6.09 (s, 2H, CH_2), 7.47 (dd, J = 7.4, 4.6 Hz, 1H, H-5'), 7.66 (d, J = 7.6 Hz, 1H, H-3'), 7.78 (q, J = 8.0 Hz, 4H, H-2", H-3", H-5", H-6"), 7.95 (td, J = 7.5, 1.8 Hz, 1H, H-4'), 8.60 (dt, J = 4.7, 1.2 Hz, 1H, H-6'), 9.31 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 38.9 (CH_3-trz), 57.2 (CH_2), 121.5 (C-1"), 123.3 (C-3'), 124.1 (C-5'), 129.5 (C-3", C-5"), 129.9 (C-5), 131.3 (C-2", C-6"), 136.5 (C-4"), 137.7 (C-4'), 141.5 (C-4), 149.7 (C-6'), 151.9 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.1 (d, J = 712 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –144 (septet, J = 712 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{15}H_{14}ClN_4^+$ $[M]^+$ = 285.0902, found 285.0903. Anal. calcd for $C_{15}H_{14}ClF_6N_4P$: C 41.83, H 3.28, N 13.01; found: C 41.55, H 3.02, N 12.71.

4-(Pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium salts 2B



2B PF_6

3-Methyl-1-phenyl-4-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Ba PF_6, R = H): Compound **4Ba 2OTf** (580 mg, 1.00 mmol), EtOH (10 mL), $Mo(CO)_6$ (396.0 mg, 1.50 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (388.3 mg, 98%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.6. Mp 118–120 °C. IR: 3173, 2855, 1723, 1595, 1503, 1471, 1435, 1275, 1150, 877, 828, 767, 680 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.40 (s, 3H, CH_3-trz), 4.63 (s, 2H, CH_2), 7.38 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H, H-5'), 7.56 (d, J = 7.8 Hz, 1H, H-3'), 7.73 (m, 3H, H-3", H-4", H-5"), 7.88 (td, J = 7.7, 1.9 Hz, 1H, H-4'), 8.01 (dd, J = 7.7, 2.0 Hz, 2H, H-

2", H-6"), 8.55 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H, H-6'), 9.42 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 30.8 (CH_2), 38.3 (CH_3-trz), 121.5 (C-2", C-6"), 122.8 (C-5'), 123.6 (C3'), 127.7 (C-5), 130.3 (C-3", C-5"), 131.7 (C-4"), 134.7 (C-1"), 137.5 (C-4'), 142.6 (C-4), 149.5 (C-6'), 154.2 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.1 (d, *J* = 711 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, *J* = 711 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{15}H_{15}N_4^+$ $[M]^+$ = 251.1291, found 251.1289. Anal. calcd for $C_{15}H_{15}F_6N_4P \times 1/8\ H_2O$: C 45.21, H 3.84, N 14.06; found: C 44.82, H 3.45, N 13.79.

1-(4-Methoxyphenyl)-3-methyl-4-(pyridin-2-ylmethyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Bc PF_6, R = OMe): Compound **4Bc 2OTf** (610 mg, 1.0 mmol), EtOH (10 mL), $Mo(CO)_6$ (396.0 mg, 1.5 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.0 mmol). White solid (233.9 mg, 90%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.6. Mp 117–119. IR: 3173, 1594, 1515, 1484, 1437, 1416, 1255, 1176, 1025, 828, 756 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.87 (s, 3H, OCH_3), 4.36 (s, 3H, CH_3-trz), 4.61 (s, 2H, CH_2), 7.25 (d, *J* = 9.1 Hz, 2H, H-3", H-5"), 7.38 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H, H-5'), 7.56 (d, *J* = 7.8 Hz, 1H, H-3'), 7.88 (td, *J* = 7.7, 1.9 Hz, 1H, H-4'), 7.93 (d, *J* = 9.0 Hz, 2H, H-2", H-6"), 8.55 (d, *J* = 4.2 Hz, 1H, H-6'), 9.32 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 30.7 (CH_2), 39.2 (CH_3-trz), 55.9 (OCH_3), 115.3 (C-3", C-5"), 122.8 (C-5'), 123.1 (C-2", C-6"), 123.6 (C-3'), 127.4 (C-5), 127.8 (C-1"), 137.6 (C-4'), 142.4 (C-4), 149.4 (C-6'), 154.2 (C-2'), 161.3 (C-4"). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –70.1 (d, *J* = 711 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, *J* = 711 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{17}N_4O^+$ $[M]^+$ = 281.1397, found 281.1398. Anal. calcd for $C_{16}H_{17}F_6N_4OP \times 1/2\ H_2O$: C 44.15, H 4.17, N 12.87; found: C 43.78, H 3.84, N 12.57.

3-Methyl-4-(pyridin-2-ylmethyl)-1-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazolium hexafluorophosphate(V) (2Be PF_6, R = CF_3): Compound **4Be 2OTf** (648 mg, 1.0 mmol), EtOH (10 mL), $Mo(CO)_6$ (396.0 mg, 1.5 mmol). H_2O (10 mL), KPF_6 (368 mg, 2.00 mmol). White solid (450.1 mg, 97%). R_f (CH_2Cl_2 : MeOH = 5 : 1) = 0.6. Mp 150–151. IR: 3176, 1727, 1618, 1592, 1571, 1484, 1418, 1324, 1175, 1129, 1066, 1022, 999, 825, 760 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.43 (s, 3H, CH_3-trz), 4.65 (s, 2H, CH_2), 7.39 (ddd, *J* = 7.6, 4.9, 1.1 Hz, 1H, H-5'), 7.56 (d, *J* = 7.8 Hz, 1H, H-3'), 7.89 (td, *J* = 7.7, 1.9 Hz, 1H, H-4'), 8.15 (d, *J* = 8.5 Hz, 2H, H-3", H-5"), 8.26 (d, *J* = 8.5 Hz, 2H, H-2", H-6"), 8.56 (ddd, *J* = 5.0, 1.9, 1.0 Hz, 1H, H-6'), 9.53 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 31.3 (CH_2), 39.1 (CH_3-trz), 123.0 (C-2", C-6"), 123.3 (C-5'), 123.5 (q, *J* = 273 Hz, CF_3), 124.1 (C-3'), 127.6 (q, *J* = 4 Hz, C-3", C-5"),

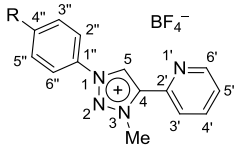
128.1 (C-5), 131.4 (q, J = 33 Hz, C-4''), 132.0 (C-4'), 138.1 (C-1''), 143.3 (C-4), 150.0 (C-6'), 154.6 (C-2'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –61.3 (s, 3F, CF_3), -70.1 (d, J = 711 Hz, 6F, PF_6). ^{31}P NMR (202 MHz, DMSO-d_6): δ = –146 (septet, J = 711 Hz, 1P, PF_6). HRMS (ESI+): calcd for $C_{16}H_{14}F_3N_4^+$ $[M]^+$ = 319.1165, found 319.1160. Anal. calcd for $C_{16}H_{14}F_9N_4P$: C 41.39, H 3.04, N 12.07; found: C 41.55, H 2.88, N 11.95.

One-pot telescoped alkylation and N–O bond cleavage at 3D into 2D BF_4 (Scheme 6)

General procedure

A mixture of pyridine *N*-oxide **3D** and Me_3OBF_4 in dry CH_2Cl_2 was flushed with argon and stirred at room temperature for the time indicated below (reaction time). The reaction mixture was concentrated using rotary evaporator. The residue was dissolved in abs. EtOH and $Mo(CO)_6$ was added. The reaction mixture was heated under reflux for 1 h. The solvents were removed and the residue was column chromatographed on silica gel using CH_2Cl_2 : MeOH (10 : 1, $R_f \approx$ 0.6), affording pure pyridyl-triazolim salt **2D BF_4**.

For quantities used in the above procedure, analytical and spectral data of **2D BF_4**, see below. For combustion analyses, **2D BF_4** was transformed into **2D PF_6**, as follows. KPF_6 (0.5 mmol) was added into a water (10 mL) solution of **2D BF_4** (0.25 mmol). Precipitated **2D PF_6** (50–90% based on **2D BF_4**) was collected by filtration and dried.



2D BF_4

3-Methyl-1-phenyl-4-(pyridin-2-yl)-1*H*-1,2,3-triazolium tetrafluoroborate (2Da BF_4, R = H): Compound **3Da** (238.0 mg, 1.00 mmol), Me_3OBF_4 (588.0 g, 4.00 mmol), CH_2Cl_2 (3 mL), reaction time = 4 days. EtOH (40 mL), $Mo(CO)_6$ (264.0 g, 1.00 mmol). White solid (220.0 g, 85%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.6. Mp 208–209 °C. IR: 3124, 1592, 1579, 1501, 1470, 1458, 1287, 1259, 1050, 1035, 788, 766, 741, 687, 678, 670 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.70 (s, 3H, CH_3-trz), 7.72 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H, H-5'), 7.80 (m, 3H, H-3'', H-4'', H-5''), 8.08 (dd, J = 8.4, 1.4 Hz, 2H, H-2'', H-6''), 8.15 (dt, J = 7.9, 1.2 Hz, 1H, H-3'), 8.22 (td, J = 7.7, 1.8 Hz, 1H, H-4'), 8.91 (ddd, J = 4.7, 1.7, 0.9 Hz, 1H, H-6'), 10.18 (s, 1H, H-5). ^{13}C NMR

(126 MHz, DMSO-d_6): δ = 41.2 (CH_3-trz), 121.4 (C-2", C-6"), 124.6 (C-3'), 126.0 ($C_{5'}$), 128.0 (C-5), 130.5 (C-3", C-5"), 131.9 (C-4"), 134.7 (C-1"), 138.4 (C-4'), 140.8 (C-4), 143.1 (C-2'), 150.2 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –148.3 (d, *J* = 26 Hz, 4F, BF_4). ^{11}B NMR (160 MHz, DMSO-d_6): δ = –1.3 (s, 1B, BF_4). HRMS (ESI+): calcd for $C_{14}H_{13}N_4^+$ $[M]^+$ = 237.1135, found 237.1135. Anal. calcd for $C_{14}H_{13}F_6N_4P$ (**2Da PF_6** as white solid): C 43.99, H 3.43, N 14.66; found: C 44.01, H 3.34, N 14.53. Spectral data in agreement with the literature.[2]

3-Methyl-4-(pyridin-2-yl)-1-(*p*-tolyl)-1*H*-1,2,3-triazolium tetrafluoroborate (2Db BF_4, R = CH_3): Compound **3Db** (252.0 mg, 1.00 mmol), Me_3OBF_4 (588.0 g, 4.00 mmol), CH_2Cl_2 (3 mL), reaction time = 3 days. EtOH (4 mL), $Mo(CO)_6$ (264.0 g, 1.00 mmol). White solid (332.0 mg, 98%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.6. Mp 219–220 °C. IR: 3129, 1723, 1592, 1576, 1515, 1462, 1340, 1325, 1259, 1029, 814, 786, 742, 690, 624 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.47 (s, 3H, CH_3), 4.69 (s, 3H, CH_3-trz), 7.60 (d, *J* = 7.7 Hz, 2H, H-3", H-5"), 7.71 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H, H-5'), 7.96 (dd, *J* = 8.5, 1.4 Hz, 2H, H-2", H-6"), 8.14 (dt, *J* = 7.9, 1.1 Hz, 1H, H-3'), 8.21 (td, *J* = 7.8, 1.8 Hz, 1H, H-4'), 8.90 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 1H, H-6'), 10.14 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 20.8 (CH_3), 41.2 (CH_3-trz), 121.1 (C-2", C-6"), 124.5 (C-3'), 126.0 (C-5'), 127.8 (C-5), 130.8 (C-3", C-5"), 132.4 (C-1"), 138.4 (C-4'), 140.8 (C-4), 142.1 (C-4"), 143.1 (C-2'), 150.1 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –148.3 (d, *J* = 26 Hz, 4F, BF_4). ^{11}B NMR (160 MHz, DMSO-d_6): δ = –1.3 (s, 1B, BF_4). HRMS (ESI+): calcd for $C_{15}H_{15}N_4^+$ $[M]^+$ = 251.1291, found 251.1288. Anal. calcd for $C_{15}H_{15}F_6N_4P$ (**2Db PF_6** as white solid): C 45.46, H 3.82, N 14.14; found: C 45.71, H 3.70, N 14.03.

1-(4-Methoxyphenyl)-3-methyl-4-(pyridin-2-yl)-1*H*-1,2,3-triazolium tetrafluoroborate (2Dc BF_4, R = OMe): Compound **3Dc** (268.0 mg, 1.00 mmol), Me_3OBF_4 (588.0 mg, 4.00 mmol), CH_2Cl_2 (5 mL), reaction time = 7 days. EtOH (20 mL), $Mo(CO)_6$ (264.0 mg, 1.00 mmol). White solid (230.1 mg, 65%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.6. Mp 194–196 °C. IR: 3130, 1722, 1611, 1578, 1517, 1461, 1438, 1325, 1269, 1178, 1019, 825, 785, 741, 690, 608 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.90 (s, 3H, OCH_3), 4.67 (s, 3H, CH_3-Ntrz), 7.32 (d, *J* = 9.1 Hz, 2H, H-3", H-5"), 7.71 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H, H-5'), 8.00 (d, *J* = 9.1 Hz, 2H, H-2", H-6"), 8.13 (dt, *J* = 7.9, 1.1 Hz, 1H, H-3'), 8.20 (td, *J* = 7.8, 1.8 Hz, 1H, H-4'), 8.90 (dt, *J* = 4.7, 1.4 Hz, 1H, H-6'), 10.07 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 41.0 (CH_3-trz), 55.9 (OCH_3), 115.4 (C-3", C-5"), 123.0 (C-2", C-6"), 124.5 (C-3'), 126.0 (C-5'), 127.7 (C-5), 127.7 (C-1"),

(2) Bernet, L.; Lalrempuia, R.; Ghattas, W.; Mueller-Bunz, H.; Vigara, L.; Llobet, A.; Albrecht, M. *Chem. Commun.* **2011**, *47*, 8058–8060.

138.4 (C-4'), 140.6 (C-4), 143.1 (C-2'), 150.1 (C-6'), 164.4 (C-4''). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –148.3 (d, J = 26 Hz, 4F, BF_4). ^{11}B NMR (160 MHz, DMSO-d_6): δ = –1.3 (s, 1B, BF_4). HRMS (ESI+): calcd for $C_{15}H_{15}N_4O^+$ $[M]^+$ = 267.1240, found 267.1236. Anal. calcd for $C_{15}H_{15}F_6N_4OP \times 0.5H_2O$ (**2Dc PF_6** as white solid): C 42.77, H 3.73, N 13.30; found: C 42.50, H 3.34, N 13.05.

1-(4-Cyanophenyl)-3-methyl-4-(pyridin-2-yl)-1*H*-1,2,3-triazolium tetrafluoroborate (2Dd BF_4, R = CN): Compound **3Dd** (263.0 mg, 1.00 mmol), Me_3OBF_4 (588.0 mg, 4.00 mmol), CH_2Cl_2 (8 mL), reaction time = 7 days. EtOH (20 mL), $Mo(CO)_6$ (264.0 mg, 1.00 mmol). White solid (209.4 mg, 60%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.6. Mp 184–186 °C. IR: 3127, 2233, 1817, 1605, 1590, 1577, 1513, 1471, 1458, 1280, 1033, 839, 792, 686 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.73 (s, 3H, CH_3-trz), 7.73 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H, H-5'), 8.13 (dt, J = 7.9, 1.2 Hz, 1H, H-3'), 8.23 (td, J = 7.8, 1.7 Hz, 1H, H-4'), 8.32 (d, J = 3.2 Hz, 4H, H-2'', H-3'', H-5'', H-6''), 8.91 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H, H-6''), 10.28 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 41.5 (CH_3-trz), 114.4 (C-4''), 117.4 (CN), 121.6 (C-2'', C-6''), 122.3 (C-3'), 124.5 (C-5'), 126.1 (C-5), 134.7 (C-3'', C-5''), 137.5 (C-1''), 138.5 (C-4'), 141.0 (C-4), 142.9 (C-2'), 150.2 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –148.3 (d, J = 26 Hz, 4F, BF_4). ^{11}B NMR (160 MHz, DMSO-d_6): δ = –1.3 (s, 1B, BF_4). HRMS (ESI+): calcd for $C_{15}H_{12}N_5^+$ $[M]^+$ = 262.1087, found 262.1085. Anal. calcd for $C_{15}H_{12}F_6N_5P$ (**2Dd PF_6** as white solid): C 44.24, H 2.97, N 17.20; found: C 44.55, H 2.74, N 16.86.

3-Methyl-4-(pyridin-2-yl)-1-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazolium tetrafluoroborate (2De BF_4, R = CF_3): Compound **3De** (306.2 mg, 1.00 mmol), Me_3OBF_4 (588.0 mg, 4.00 mmol), CH_2Cl_2 (8 mL), reaction time = 7 days. EtOH (20 mL), $Mo(CO)_6$ (264.0 mg, 1.00 mmol). White solid (368.0 mg, 94%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.6. Mp 172–173 °C. IR: 3126, 1618, 1580, 1522, 1475, 1461, 1323, 1266, 1211, 1176, 1134, 1119, 1017, 851, 792, 744, 695, 682, 624 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.74 (s, 3H, CH_3-trz), 7.73 (ddd, J = 7.5, 4.8, 1.3 Hz, 1H, H-5'), 8.15 (dt, J = 7.9, 1.1 Hz, 1H, H-3'), 8.22 (m, 3H, H-4', H-3'', H-5''), 8.33 (d, J = 8.6 Hz, 2H, H-2'', H-6''), 8.92 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H, H-6'), 10.29 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 41.4 (CH_3-trz), 122.4 (C-2'', C-6''), 123.4 (q, J = 273 Hz, CF_3), 124.6 (C-3'), 126.1 (C-5'), 127.9 (q, J = 4 Hz, C-3'', C-5''), 128.5 (C-5), 131.6 (q, J = 33 Hz, C-4''), 137.5 (C-1''), 138.5 (C-4'), 141.0 (C-4), 142.9 (C-2'), 150.2 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –61.3 (s, 3F, CF_3), –148.3 (d, J = 26 Hz, 4F, BF_4). ^{11}B NMR (160 MHz,

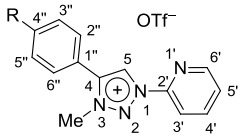
DMSO-d_6): δ = –1.3 (s, 1B, BF_4). HRMS (ESI+): calcd for $C_{15}H_{12}F_3N_4^+$ $[M]^+$ = 305.1009, found 305.1006. Anal. calcd for $C_{15}H_{12}F_9N_4P$ (**2De PF_6** as white solid): C 40.01, H 2.69, N 12.44; found: C 39.92, H 2.57, N 12.33.

1-(4-Bromophenyl)-3-methyl-4-(pyridin-2-yl)-1*H*-1,2,3-triazolium tetrafluoroborate (2Dg BF_4, R = Br): Compound **3Dg** (317.1 mg, 1.00 mmol), Me_3OBF_4 (588.0 mg, 4.00 mmol), CH_2Cl_2 (8 mL), reaction time = 7 days. EtOH (20 mL), $Mo(CO)_6$ (264.0 mg, 1.00 mmol). White solid (343 mg, 85%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.6. Mp 214–215 °C. IR: 3134, 1788, 1722, 1579, 1497, 1462, 1259, 1029, 1014, 832, 787, 743, 622 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.70 (s, 3H, CH_3-trz), 7.72 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H, H-5'), 8.04 (d, *J* = 1.1 Hz, 4H, H-2", H-3", H-5", H-6"), 8.13 (dt, *J* = 7.8, 1.1 Hz, 1H, H-3'), 8.22 (td, *J* = 7.8, 1.8 Hz, 1H, H-4'), 8.90 (dt, *J* = 4.6, 1.6 Hz, 1H, H-6'), 10.19 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 41.3 (CH_3-trz), 123.4 (C-2", C-6"), 124.5 (C-3'), 125.1 (C-1"), 126.0 (C-5'), 128.2 (C-5), 133.5 (C-3", C-5"), 133.9 (C-4"), 138.5 (C-4'), 140.9 (C-4), 142.9 (C-2'), 150.2 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –148.3 (d, *J* = 26 Hz, 4F, BF_4). ^{11}B NMR (160 MHz, DMSO-d_6): δ = –1.3 (s, 1B, BF_4). HRMS (ESI+): calcd for $C_{14}H_{12}BrN_4^+$ $[M]^+$ = 315.0240, found 315.0237. Anal. calcd for $C_{14}H_{12}BrF_6N_4P$ (**2Dg PF_6** as white solid): C 36.46, H 2.62, N 12.15; found: C 36.54, H 2.55, N 11.99.

Methylation of pyridyl-triazoles 1A into triazoliun salts 2C (Scheme 3)

General procedure

Pyridyl-triazole **1C** in dry CH_2Cl_2 was purged with dry argon and stirred on an ice-bath at 0 °C for a few minutes. MeOTf was added via syringe and the reaction mixture was stirred for 30 min at 0 °C and then 24 h at room temperature. The reaction mixture was concentrated using rotary evaporator and the residue was column chromatographed on silicagel using a mixture of CH_2Cl_2 and MeOH (10 : 1) as eluent (R_f ≈ 0.3). Re-crystallization from EtOAc-light petroleum afforded analytically pure triazoliun salts **2C OTf**. Quantities used in the above procedure, analytical and spectral data of **2C OTf** are given below.



2C OTf

3-Methyl-4-phenyl-1-(pyridin-2-yl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2Ca OTf, R = H): Compound **1Ca** (222.0 mg, 1.00 mmol), CH_2Cl_2 (3 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (310.0 g, 80%). R_f (CH_2Cl_2 : MeOH = 10:1) = 0.3. Mp 128–129 °C. IR: 3099, 1613, 1598, 1572, 1260, 1222, 1194, 1146, 1079, 1050, 793, 772, 752, 698, 634 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.44 (s, 3H, CH_3-trz), 7.62 (m, 4H, H-5', H-3", H-5", H-4"), 7.75 (d, *J* = 8.2 Hz, 2H, H-2", H-6"), 8.09 (td, *J* = 7.9, 1.7 Hz, 1H, H-4'), 8.23 (d, *J* = 8.3 Hz, 1H, H-3'), 8.60 (ddd, *J* = 4.5, 1.8, 0.8 Hz 1H, H-6'), 9.04 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 39.4 (CH_3-trz), 115.6 (C-3'), 121.7 (C-1"), 124.4 (C-5), 127.1 (C-5'), 129.8 (C-2", C-6"), 129.8 (C-3", C-5"), 132.2 (C-4", 140.5 (C-4'), 144.4 (C-4), 146.6 (C-2'), 149.2 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –78.4 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{14}H_{13}N_4^+$ $[M]^+$ 237.1135, found 237.1134. Anal. calcd for $C_{15}H_{13}F_3N_4O_3S$: C 46.63, H 3.39, N 14.50; found: C 46.68, H 3.09, N 14.52.

3-Methyl-1-(pyridin-2-yl)-4-(*p*-tolyl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2Cb OTf, R = CH_3): Compound **1Cb** (236.0 mg, 1.00 mmol), CH_2Cl_2 (3 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (322.7 mg, 81%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.3. Mp 128–129 °C. IR: 3105, 1616, 1508, 1473, 1256, 1224, 1192, 1153, 1029, 1000, 821, 786, 637 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3H, CH_3), 4.43 (s, 3H, CH_3-trz), 7.41 (d, *J* = 7.8, 2H, H-3", H-5"), 7.62 (m, 3H, H-2", H-6", H-5'), 8.09 (td, *J* = 7.9, 1.8 Hz, 1H, H-4'), 8.24 (dt, *J* = 8.2, 0.9 Hz, 1H, H-3'), 8.60 (ddd, *J* = 4.7, 1.9, 0.9 Hz, 1H, H-6'), 9.01 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.6 (CH_3), 39.4 (CH_3-trz), 115.6 (C-3'), 118.7 (C-1"), 124.2 (C-5), 127.0 (C-5'), 129.6 (C-2", C-6"), 130.5 (C-3", C-5"), 140.5 (C-4'), 142.9 (C-4"), 144.6 (C-4), 146.6 (C-2'), 149.1 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{15}H_{15}N_4^+$ $[M]^+$ 251.1291, found 251.1291. Anal. calcd for $C_{16}H_{15}F_3N_4O_3S$: C 48.00, H 3.78, N 13.99; found: C 47.96, H 3.87, N 14.05.

4-(4-Methoxyphenyl)-3-methyl-1-(pyridin-2-yl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2Cc OTf, R = OMe): Compound **1Cc** (252.0 mg, 1.00 mmol), CH_2Cl_2 (3 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (313 mg, 75%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.3. Mp 127–128 °C. IR: 3099, 1613, 1508, 1473, 1454, 1259,

1184, 1143, 1032, 1019, 836, 780, 635 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.89 (s, 3H, OCH_3), 4.42 (s, 3H, CH_3-trz), 7.10 (d, *J* = 8.7 Hz, 2H, H-3", H-5"), 7.61 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H, H-5'), 7.68 (d, *J* = 8.7 Hz, 2H, H-2", H-6"), 8.09 (td, *J* = 7.9, 1.8 Hz, 1H, H-4'), 8.21 (d, *J* = 8.2 Hz, 1H, H-3'), 8.60 (ddd, *J* = 4.9, 1.9, 0.9 Hz 1H, H-6'), 9.01 (s, 1H, H-5). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 39.3 (CH_3-trz), 55.6 (OCH_3), 113.4 (C-3'), 115.3 (C-3", C-5"), 115.4 (C-1"), 123.9 (C-5), 127.0 (C-5'), 131.3 (C-2", C-6"), 140.5 (C-4'), 144.4 (C-4), 146.6 (C-2'), 149.2 (C-6'), 162.5 (C-4"). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{15}H_{15}N_4O^+$ $[M]^+$ 267.1240, found 267.1240. Anal. calcd for $C_{16}H_{15}F_3N_4O_4S$: C 44.15, H 3.63, N 13.46; found: C 45.96, H 3.50, N 13.51.

4-(4-Cyanophenyl)-3-methyl-1-(pyridin-2-yl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2Cd OTf, R = CN): Compound **1Cd** (247.0 mg, 1.00 mmol), CH_2Cl_2 (4 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (331.6 mg, 81%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.3. Mp 150–153 °C. IR: 3128, 2230, 1617, 1503, 1262, 1222, 1194, 1157, 1080, 1031, 846, 837, 634 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.48 (s, 3H, CH_3-trz), 7.86 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H, H-5'), 8.07 (d, *J* = 8.4 Hz, 2H, H-2", H-6"), 8.22 (d, *J* = 8.4 Hz, 2H, H-3", H-5"), 8.27 (dt, *J* = 8.1, 0.9 Hz, 1H, H-3'), 8.35 (td, *J* = 7.9, 1.8 Hz, 1H, H-4'), 8.81 (ddd, *J* = 4.7, 1.8, 0.8 Hz, 1H, H-6'), 10.09 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.5 (CH_3-trz), 114.2 (C-4"), 115.1 (C-3'), 118.0 (CN), 126.8 (C-5), 126.9 (C-1"), 127.5 (C-5'), 130.5 (C-2", C-6"), 133.2 (C-3", C-5"), 141.4 (C-4'), 142.0 (C-4), 146.3 (C-2'), 149.6 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{15}H_{12}N_5^+$ $[M]^+$ 262.1087, found 262.1083. Anal. calcd for $C_{16}H_{12}F_3N_5O_3S$: C 46.72, H 2.94, N 17.02; found: C 46.56, H 3.13, N 16.85.

3-Methyl-1-(pyridin-2-yl)-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2Ce OTf, R = CF_3): Compound **1Ce** (290.0 mg, 1.00 mmol), CH_2Cl_2 (3 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (337 mg, 74%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.3. Mp 167–169 °C. IR: 3076, 1618, 1600, 1451, 1333, 1262, 1155, 1121, 1074, 1032, 847, 791, 697, 638, 607 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.47 (s, 3H, CH_3-trz), 7.87 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H, H-5'), 8.10 (d, *J* = 1.9 Hz, 4H, H-2", H-3", H-5", H-6"), 8.26 (dt, *J* = 8.2, 1.0 Hz, 1H, H-3'), 8.36 (td, *J* = 7.9, 1.8 Hz, 1H, H-4'), 8.81 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H, H-6'), 10.08 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.7 (CH_3-trz), 115.1 (C-3'), 123.6 (q, *J* = 273 Hz, CF_3), 126.3 (q, *J* = 4 Hz, C-3", C-5"), 126.6 (C-1"),

126.7 (C-5), 127.5 (C-5'), 130.7 (C-2", C-6"), 131.6 (q, *J* = 32 Hz, C-4"), 141.3 (C-4'), 142.2 (C-4), 146.3 (C-2'), 149.6 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –61.5 (s, 3F, CF_3), –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{15}H_{12}F_3N_4^+$ $[M]^+$ 305.1009, found 305.1005. Anal. calcd for $C_{16}H_{12}F_6N_4O_3S$: C 42.30, H 2.66, N 12.53; found: C 42.30, H 2.85, N 12.60.

4-(4-Bromophenyl)-3-methyl-1-(pyridin-2-yl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2Cg OTf, R = Br): Compound **1Cg** (301.0 mg, 1.00 mmol), CH_2Cl_2 (4 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (397.5 mg, 86%). R_f (CH_2Cl_2 : MeOH=10:1) = 0.3. Mp 144–145 °C. IR: 3080, 1608, 1576, 1478, 1455, 1263, 1220, 1189, 1162, 1150, 1076, 1031, 1008, 779, 636 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.44 (s, 3H, CH_3-trz), 7.81 (d, *J* = 8.5, 2H, H-2", H-6"), 7.86 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H, H-5'), 7.94 (d, *J* = 8.5, 2H, H-3", H-5"), 8.24 (dt, *J* = 8.3, 1.0 Hz, 1H, H-3'), 8.34 (td, *J* = 7.9, 1.8 Hz, 1H, H-4'), 8.80 (ddd, *J* = 4.8, 1.9, 0.9 Hz, 1H, H-6'), 10.00 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.5 (CH_3-trz), 115.1 (C-3'), 121.7 (C-1"), 125.6 (C-4"), 126.1 (C-5), 127.5 (C-5'), 131.6 (C-2", C-6"), 132.4 (C-3", C-5"), 141.3 (C-4'), 142.6 (C-4), 146.3 (C-2'), 149.6 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{14}H_{12}BrN_4^+$ $[M]^+$ 315.0240, found 315.0233. Anal. calcd for $C_{14}H_{12}BrF_3N_4O_3S$: C 38.72, H 2.60, N 12.04; found: C 39.09, H 2.76, N 12.24.

3-Methyl-4-(4-nitrophenyl)-1-(pyridin-2-yl)-1*H*-1,2,3-triazolium trifluoromethanesulphonate (2Ch OTf, R = NO_2): Compound **1Ch** (272.0 mg, 1.00 mmol), CH_2Cl_2 (5 mL), MeOTf (180.4 mg, 1.10 mmol, 0.12 mL). White solid (364 mg, 83%). R_f (CH_2Cl_2 : MeOH = 10 : 1) = 0.3. Mp 168–170 °C. IR: 3084, 1527, 1451, 1346, 1261, 1223, 1160, 1032, 854, 787, 635 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.49 (s, 3H, CH_3-trz), 7.88 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H, H-5'), 8.16 (d, *J* = 8.8 Hz, 2H, H-2", H-6"), 8.28 (dd, *J* = 8.3, 1.0 Hz, 1H, H-3'), 8.37 (td, *J* = 7.9, 1.8 Hz, 1H, H-4'), 8.54 (d, *J* = 8.8 Hz, 2H, H-3", H-5"), 8.82 (ddd, *J* = 4.8, 1.8, 0.9 Hz 1H, H-6'), 10.15 (s, 1H, H-5). ^{13}C NMR (126 MHz, DMSO-d_6): δ = 39.5 (CH_3-trz), 115.1 (C-3'), 124.3 (C-3", C-5"), 126.9 (C-5), 127.6 (C-5'), 128.5 (C-1"), 131.3 (C-2", C-6"), 141.4 (C-4'), 141.7 (C-4), 146.3 (C-2'), 149.2 (C-4"), 149.6 (C-6'). ^{19}F NMR (471 MHz, DMSO-d_6): δ = –77.8 (s, 3F, OTf). HRMS (ESI+): calcd for $C_{14}H_{12}N_5O_2^+$ $[M]^+$ 282.0986, found 282.0985. Anal. calcd for $C_{15}H_{12}F_3N_5O_5S$: C 41.77, H 2.80, N 16.24; found: C 42.00, H 3.02, N 16.27.

Suzuki-Miyaura cross-coupling reaction (Scheme 7)

Into a mixture of 4-bromobenzaldehyde (555.0 mg, 3.00 mmol), phenyl boronic acid (438.9 mg, 3.60 mmol) and potassium carbonate (621.0 mg, 4.50 mmol) in water (9 mL), triazolium salt **2Aa PF$_6$** (0.12 mg, 3.00 10^{-4} mmol, 0.01 mol %) and $Pd(OAc)_2$ (0.07 mg, 3.00 10^{-4} mmol, 0.01 mol %) were added. The reaction was monitored by TLC (light petroleum : ethyl acetate = 10 : 1) and ^{1}H NMR spectroscopy. After 4 h the reaction stopped at 90% conversion as judged by integration of the aldehyde proton resonances (Figure S1). For isolation, the reaction mixture was diluted with water (60 mL) and the product was extracted with dichloromethane (5 × 90 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated on a rotary evaporator. 4-Phenylbenzaldehyde was isolated by flash column chromatography using light petroleum : ethyl acetate (10 : 1) as eluent. Colorless oil, yield 83%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44–7.39 (m, 1H), 7.47 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.63 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 2H), 10.04 (s, 1H). Spectral data are in agreement with the literature.[3]

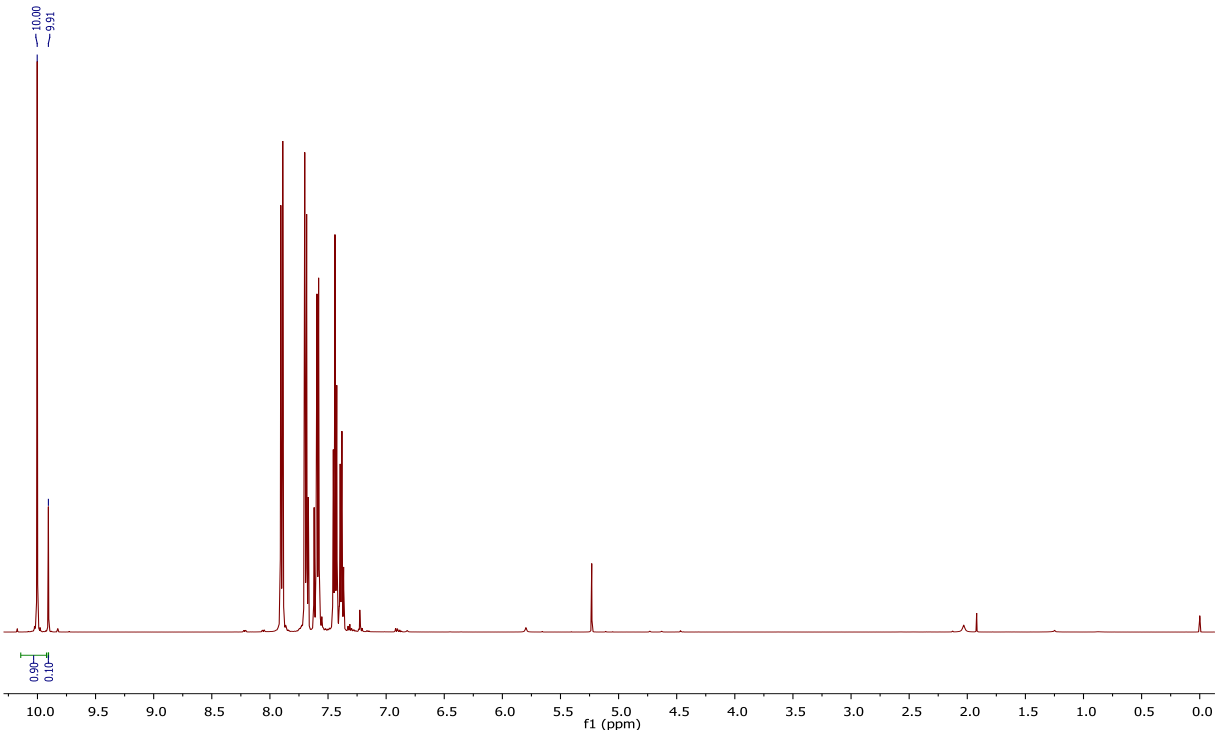
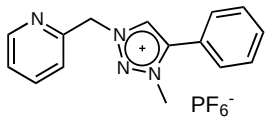


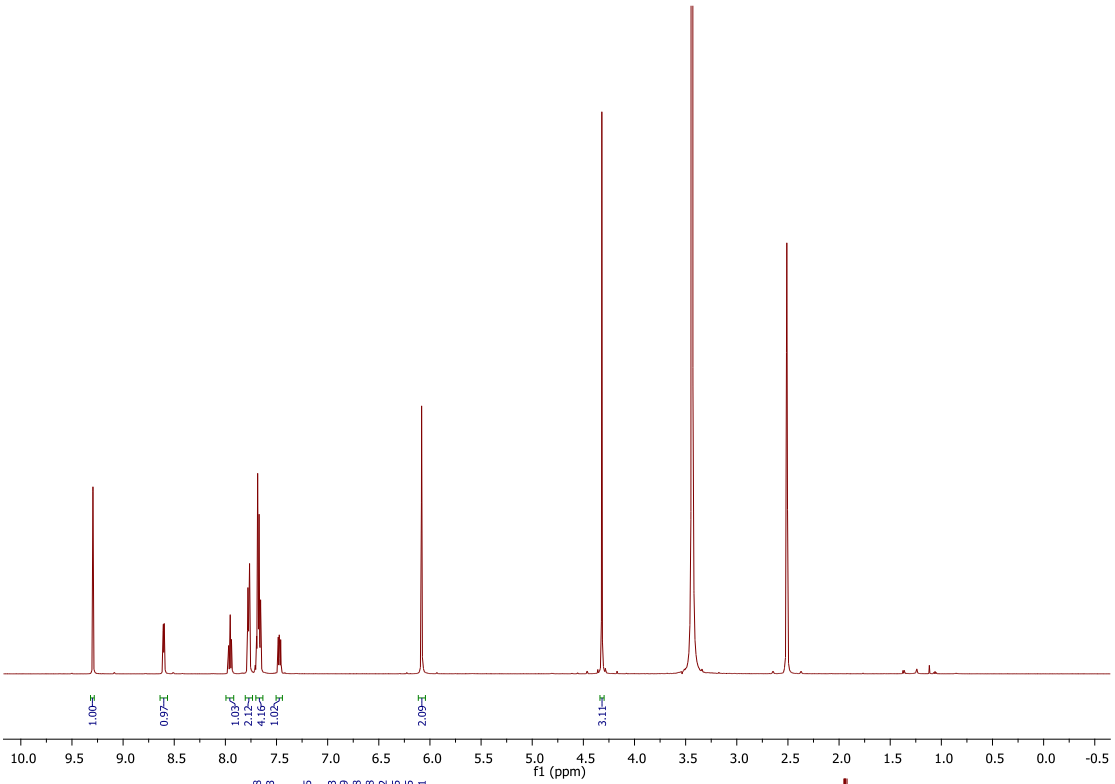
Figure S1: ^{1}H NMR spectrum in $CDCl_3$ of the aliquot from the reaction mixture of Suzuki-Miyaura cross-coupling reaction (Scheme 7) taken after 4 h and extracted into $CDCl_3$ (see text).

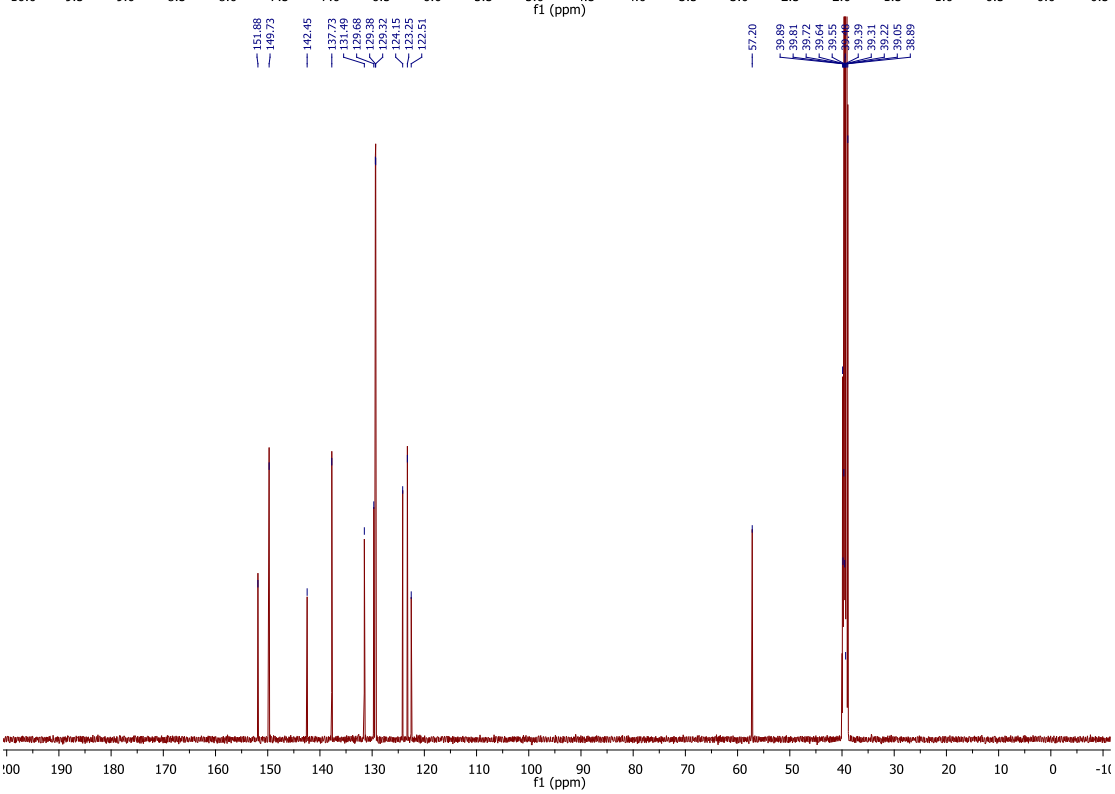
(3) Zhang, J.; Zhang, W.; Wang, J.; Zhang, M. *Adv. Synth. Catal.* **2008**, *350*, 2065–2076.

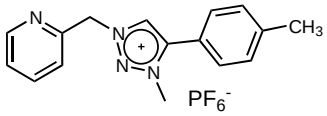
Copies of ^{1}H and ^{13}C NMR spectra



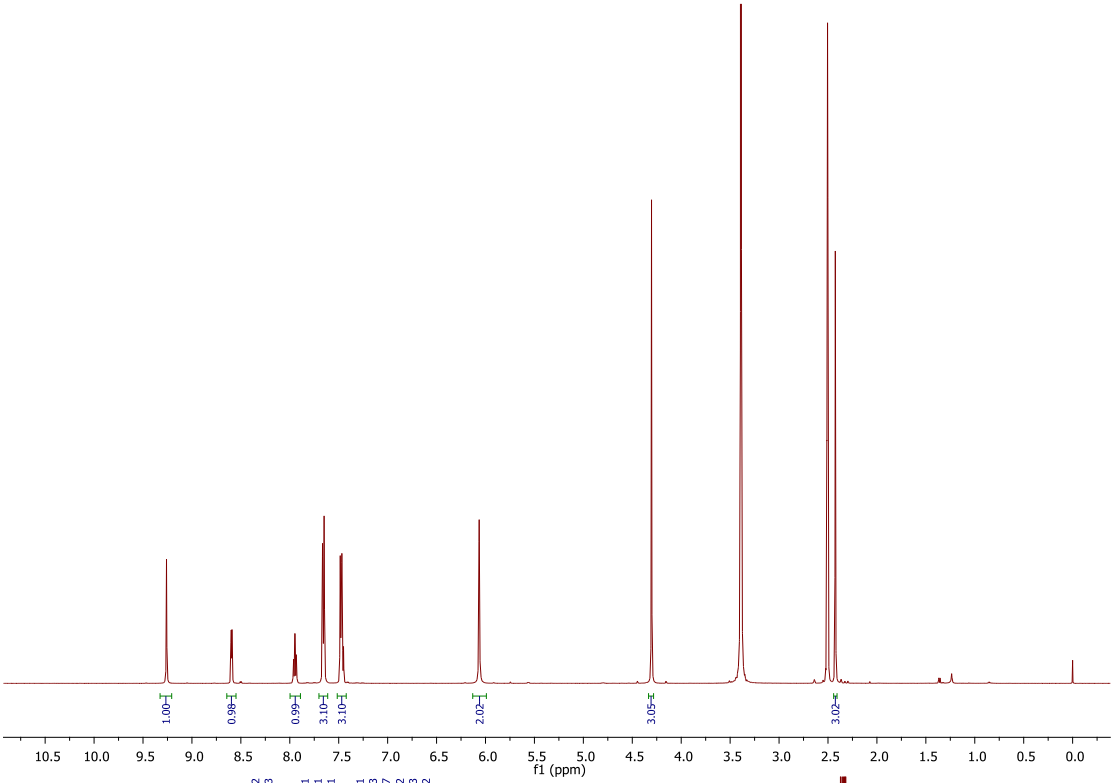
2Aa PF_6

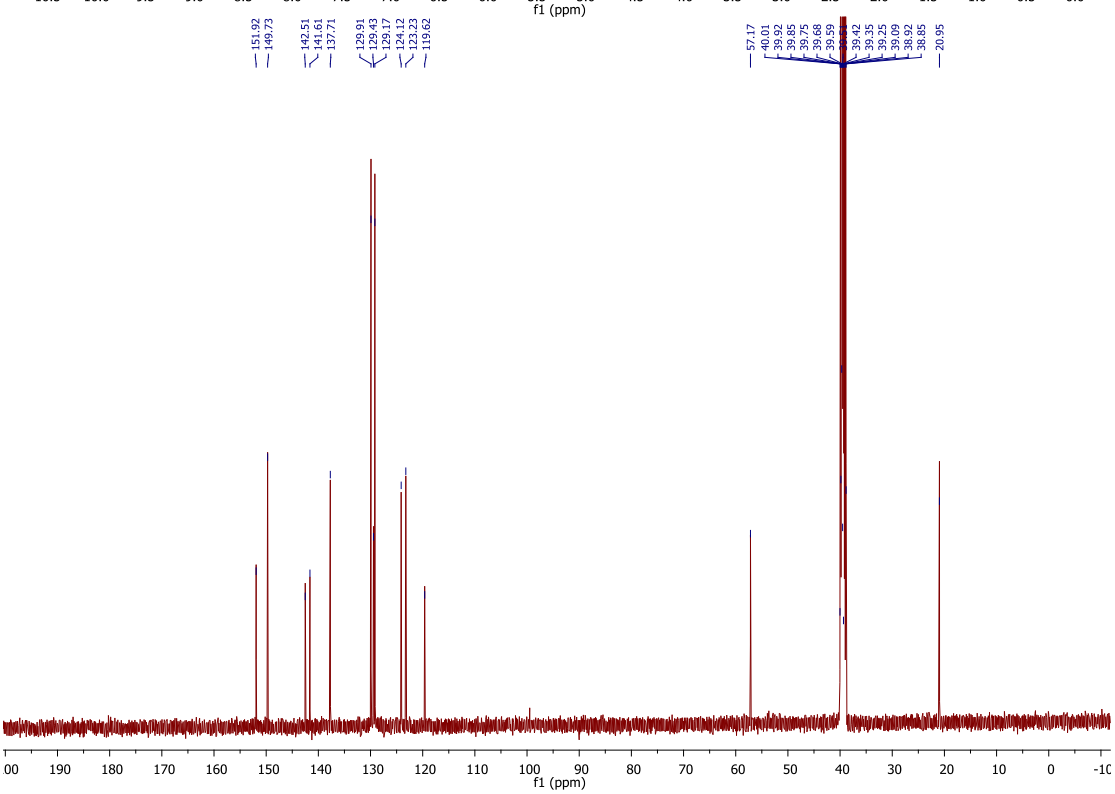


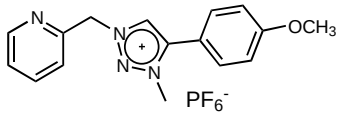



N
N
N
+
CH3
PF6-

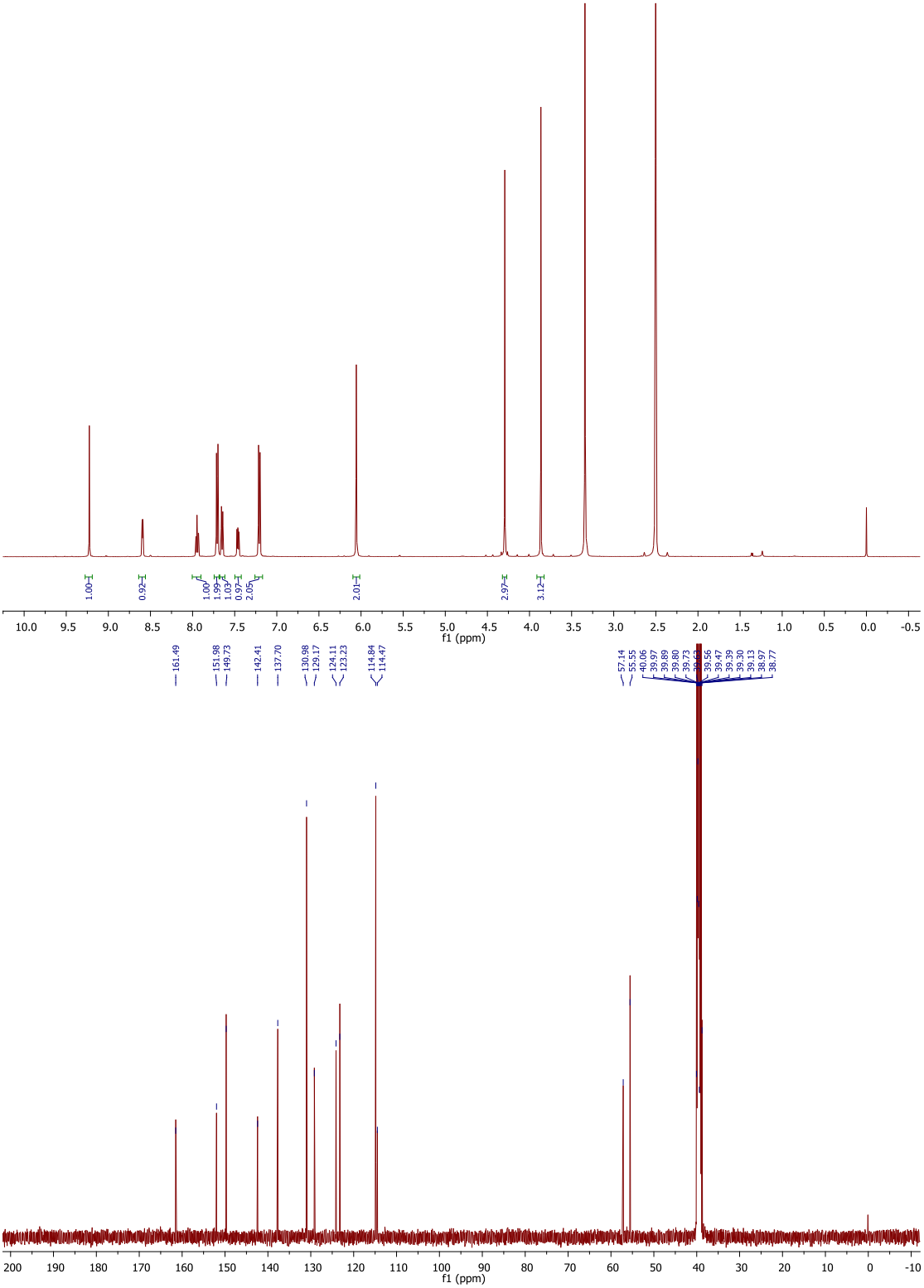
2Ab PF_6

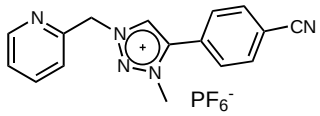

1.00
0.98
0.99
3.10
3.10
2.02
3.05
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.92
149.73
142.51
141.61
137.71
129.91
129.43
129.17
124.12
123.23
119.62
57.17
40.01
39.92
39.85
39.75
39.68
39.59
39.42
39.35
39.25
39.09
38.92
38.85
20.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

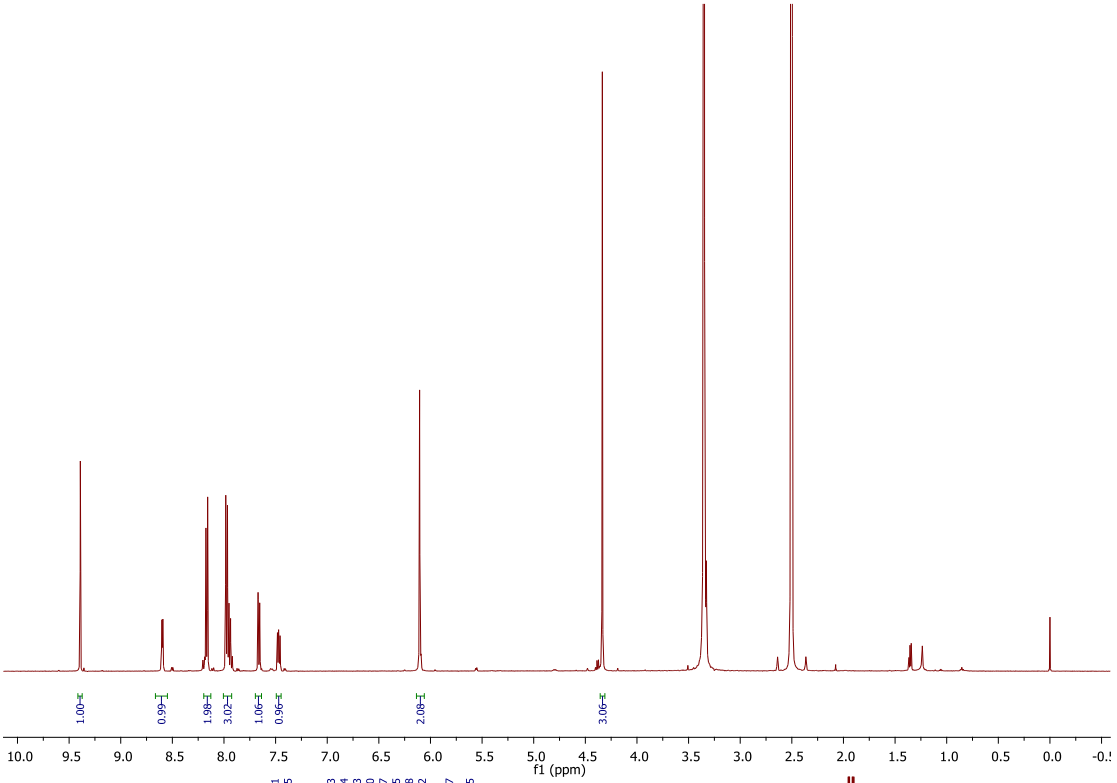

N
N
N
+
OCH3
PF6-

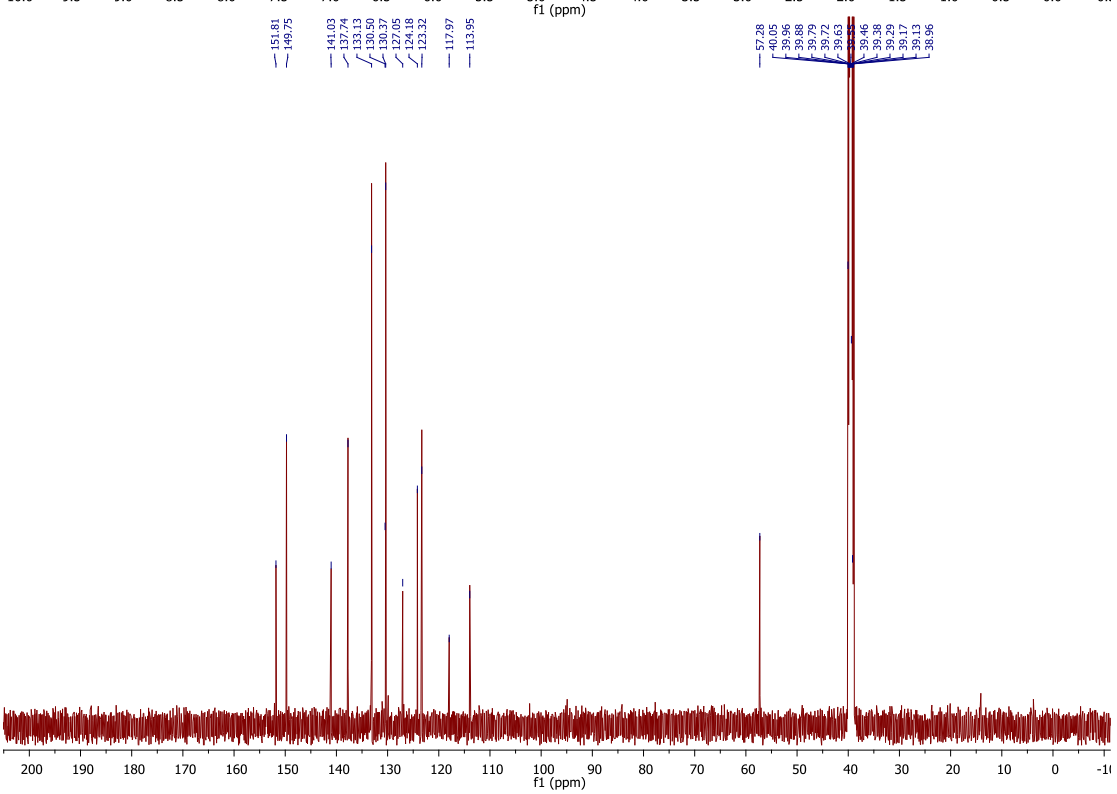
2Ac PF_6

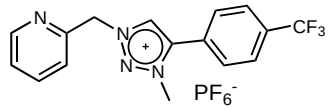

1.00
0.92
1.00
1.99
1.03
0.97
2.05
2.01
2.97
3.12
f1 (ppm)
161.49
151.98
149.73
142.41
137.70
130.98
129.17
124.11
123.23
114.84
114.47
57.14
55.55
40.06
39.97
39.89
39.80
39.73
39.63
39.56
39.47
39.39
39.30
39.13
38.97
38.77
f1 (ppm)


N
N
N
+
CN
PF6-

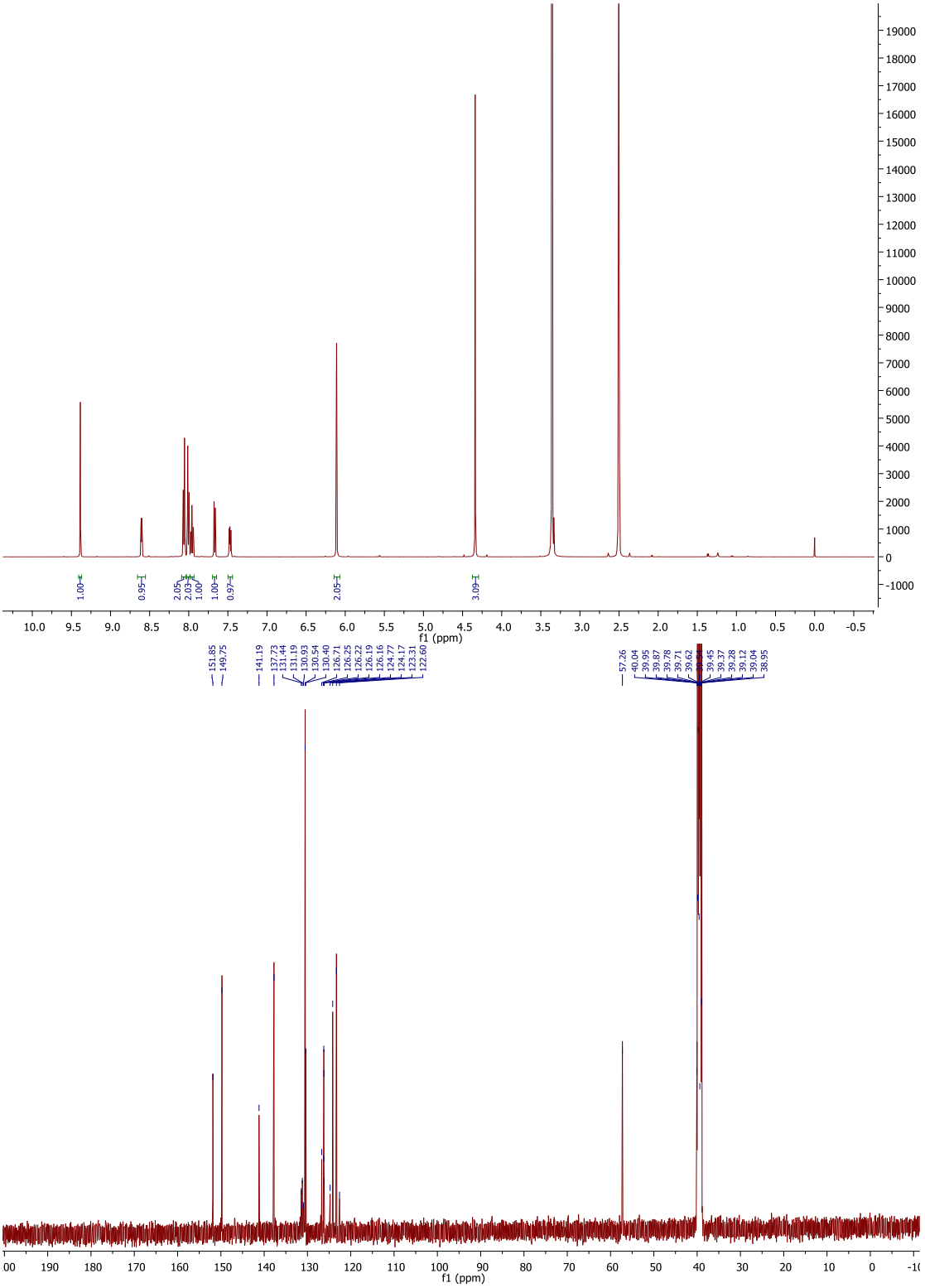
2Ad PF_6

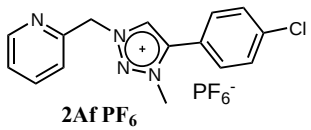

1.00
0.99
1.98
3.02
1.06
0.96
2.08
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.81
149.75
141.03
137.74
133.13
130.59
130.37
127.05
124.18
123.32
117.97
113.95
57.28
40.05
39.96
39.88
39.79
39.72
39.63
39.46
39.38
39.29
39.17
39.13
38.96
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

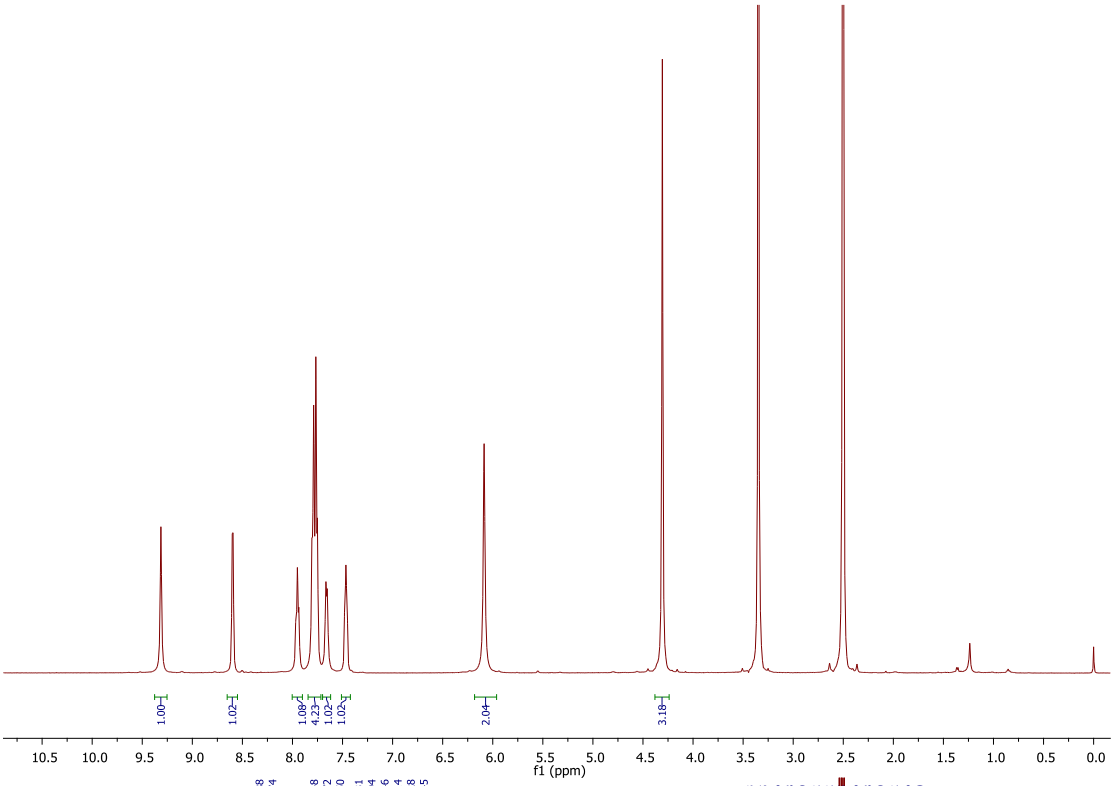

N
N
N
CF3
PF6-

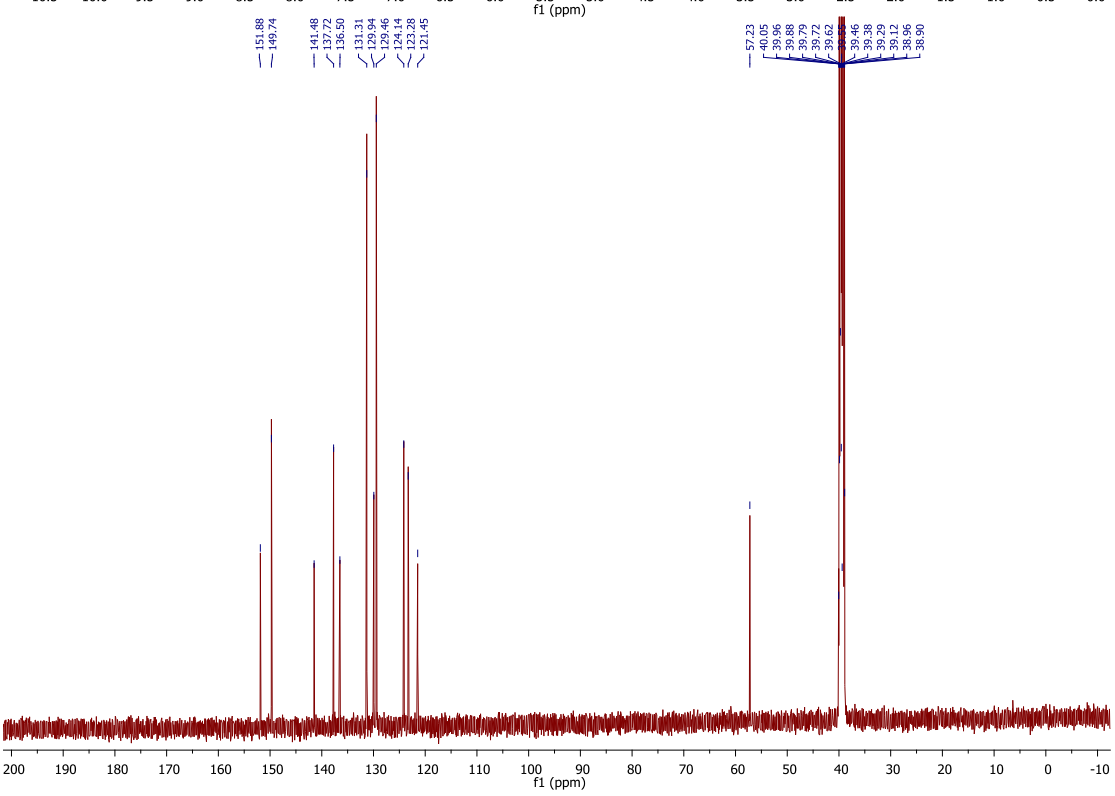
2Ae PF_6

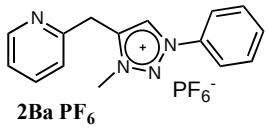

f1 (ppm)
151.85
149.75
141.19
137.23
131.44
131.19
130.93
130.54
130.40
126.71
126.25
126.22
126.19
126.16
124.77
124.17
123.31
122.60
57.26
40.04
39.95
39.87
39.78
39.71
39.62
39.45
39.37
39.28
39.12
39.04
38.95


N
N
N
Cl
PF6-

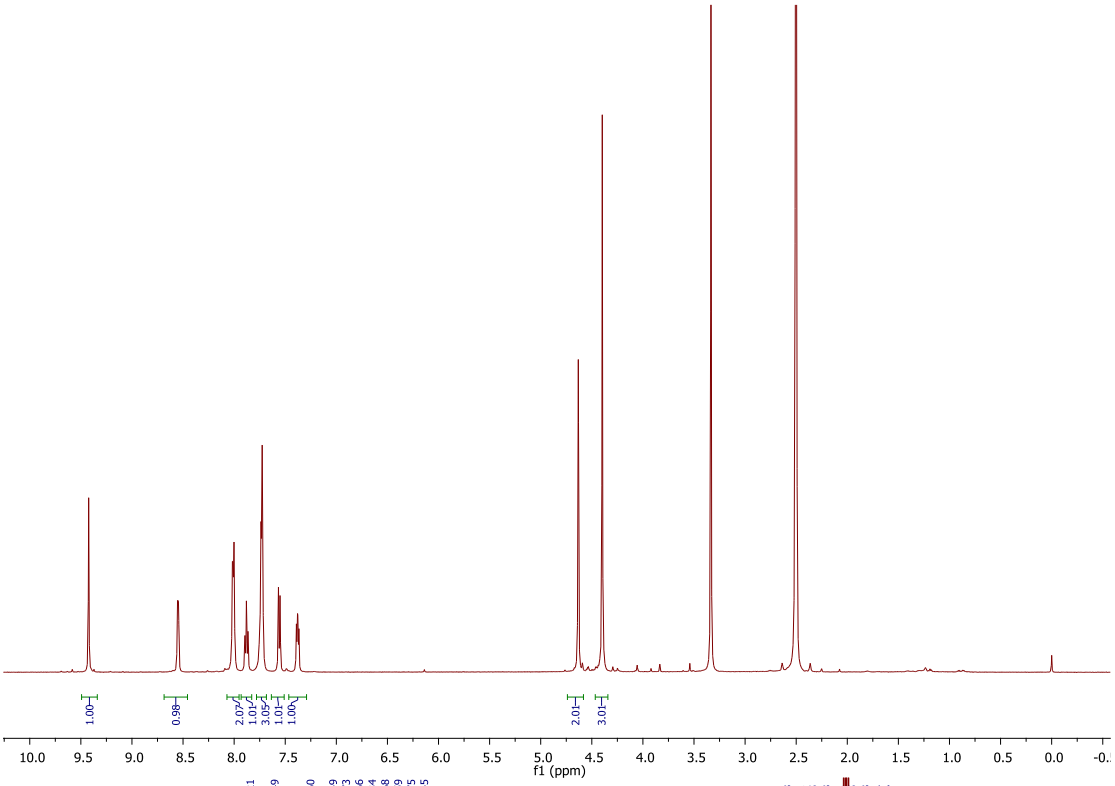
2Af PF_6

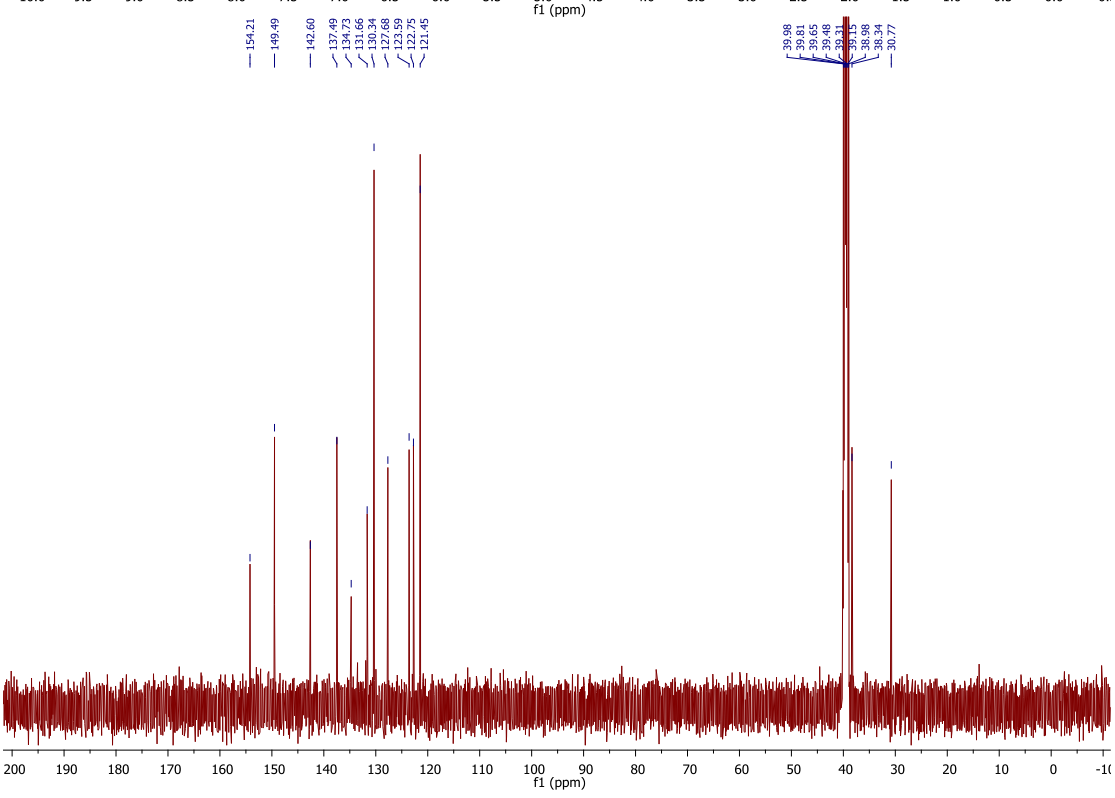

1.00
1.02
1.08
4.23
1.02
1.02
2.04
3.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

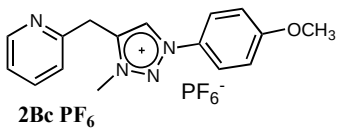

151.88
149.74
141.48
137.72
136.50
131.31
129.94
129.46
124.14
123.28
121.45
57.23
40.05
39.96
39.88
39.79
39.72
39.62
39.46
39.38
39.29
39.12
38.96
38.90
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
N
+
PF6-

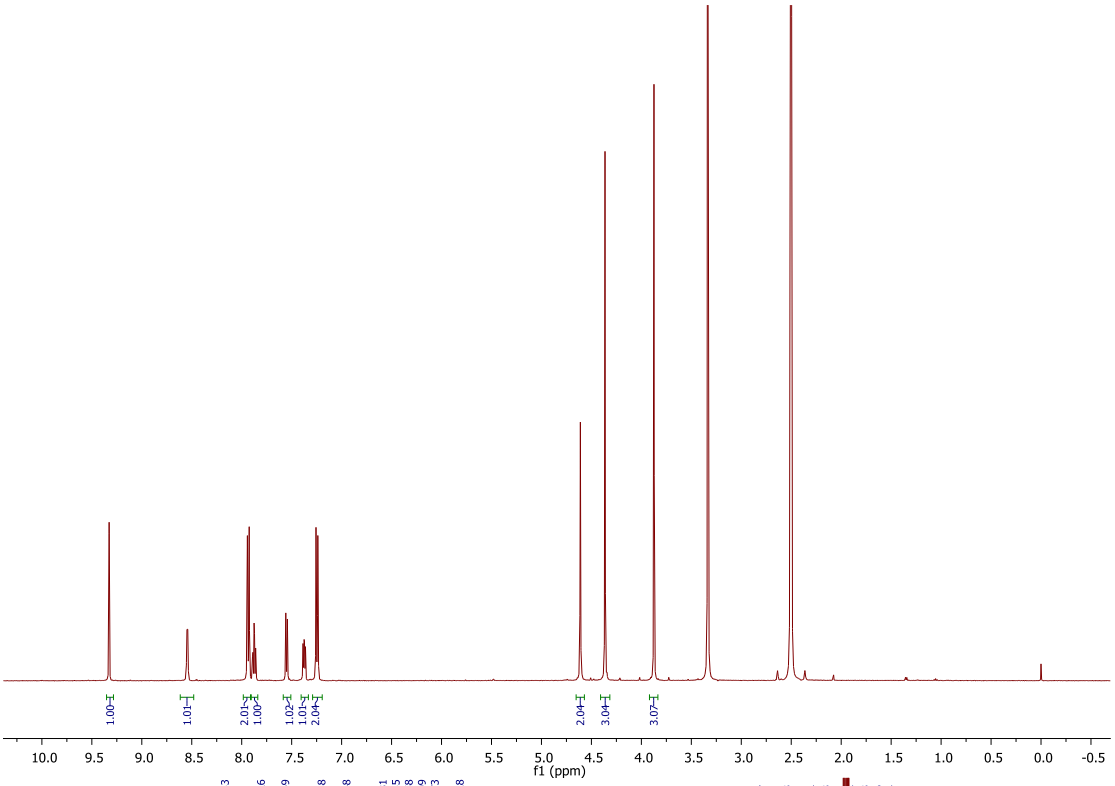
2Ba PF_6

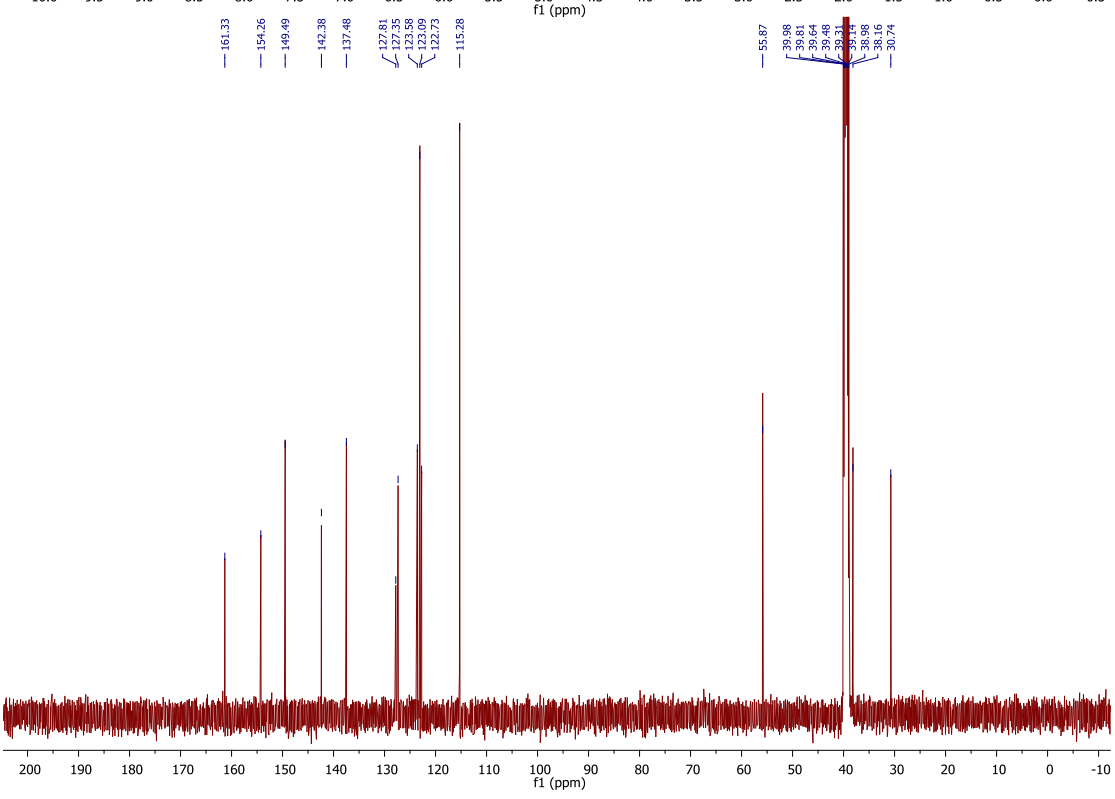

1.00
0.98
2.07
1.01
3.05
1.01
1.00
2.01
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

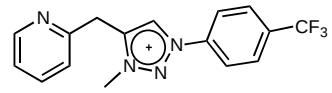

154.21
149.49
142.60
137.49
134.73
131.66
130.34
127.68
123.58
122.75
121.45
39.98
39.81
39.65
39.48
39.31
39.15
38.98
38.34
30.77
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


N
OCH3
N
N
N
PF6-

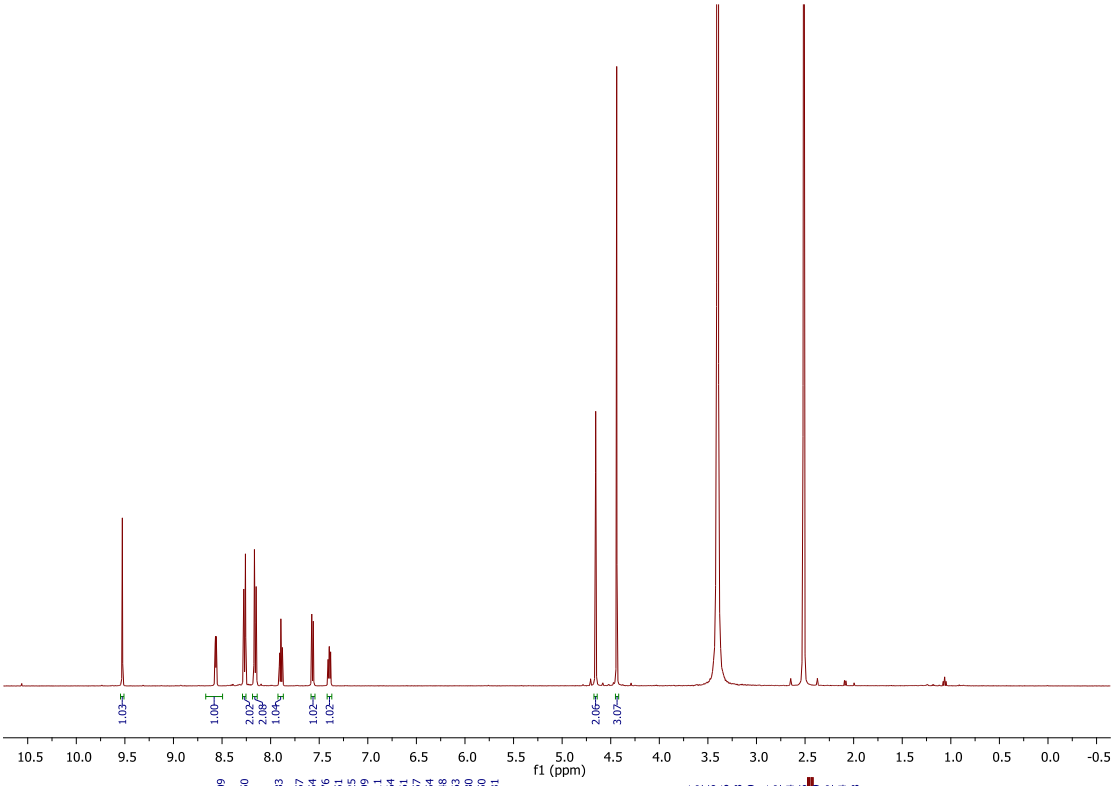
2Bc PF_6

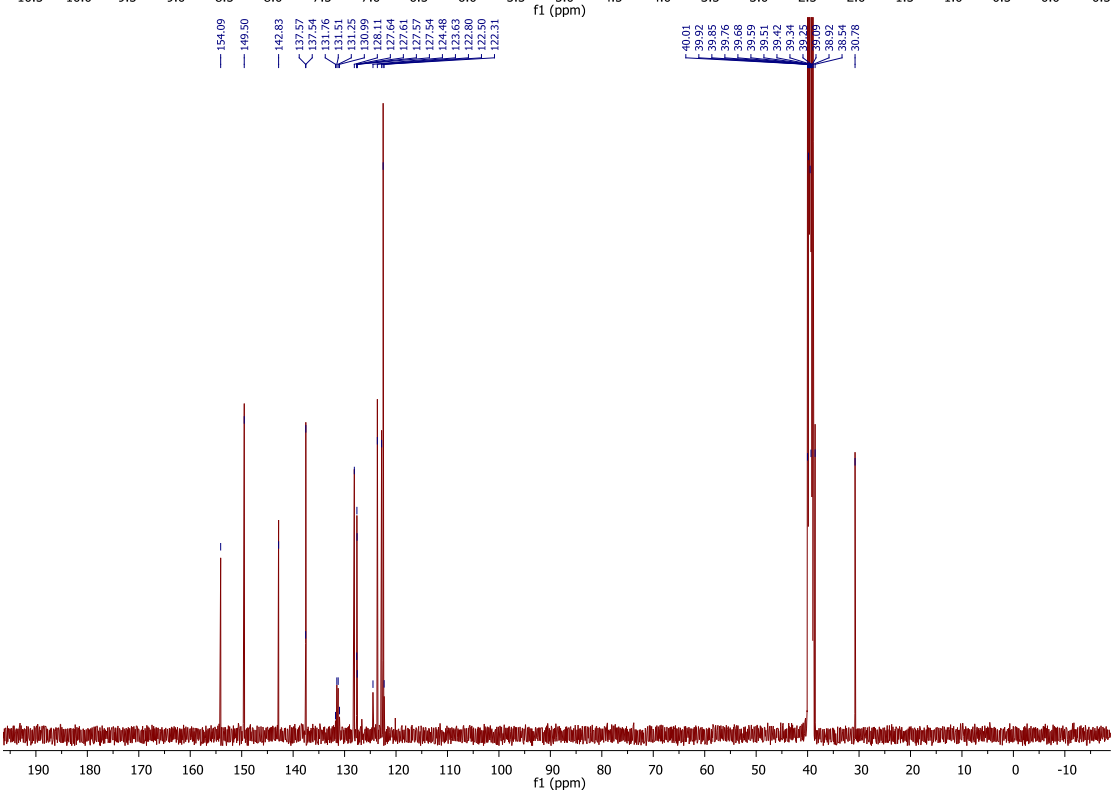

1.00
1.01
2.01
1.00
1.02
1.01
2.04
2.04
3.04
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

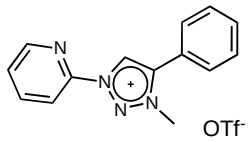

161.33
154.26
149.49
142.38
137.48
127.81
127.35
123.58
123.09
122.73
115.28
55.87
39.98
39.81
39.64
39.48
39.31
39.14
38.98
38.16
30.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
N
N
+
CF3
PF6-

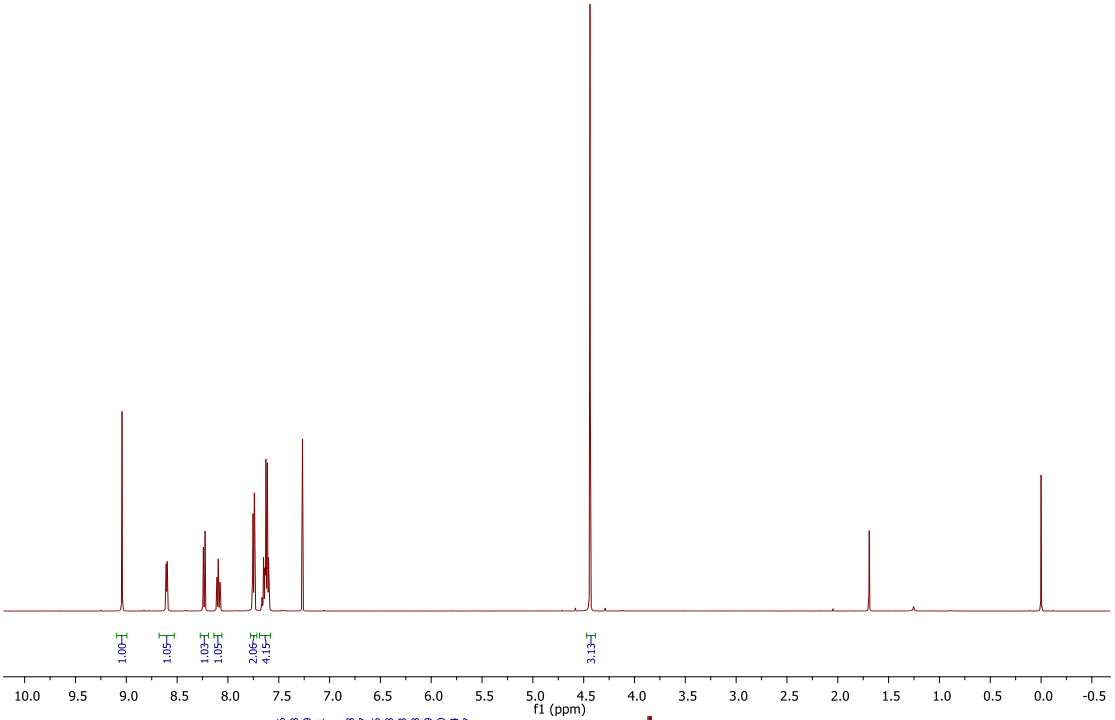
2Be PF_6

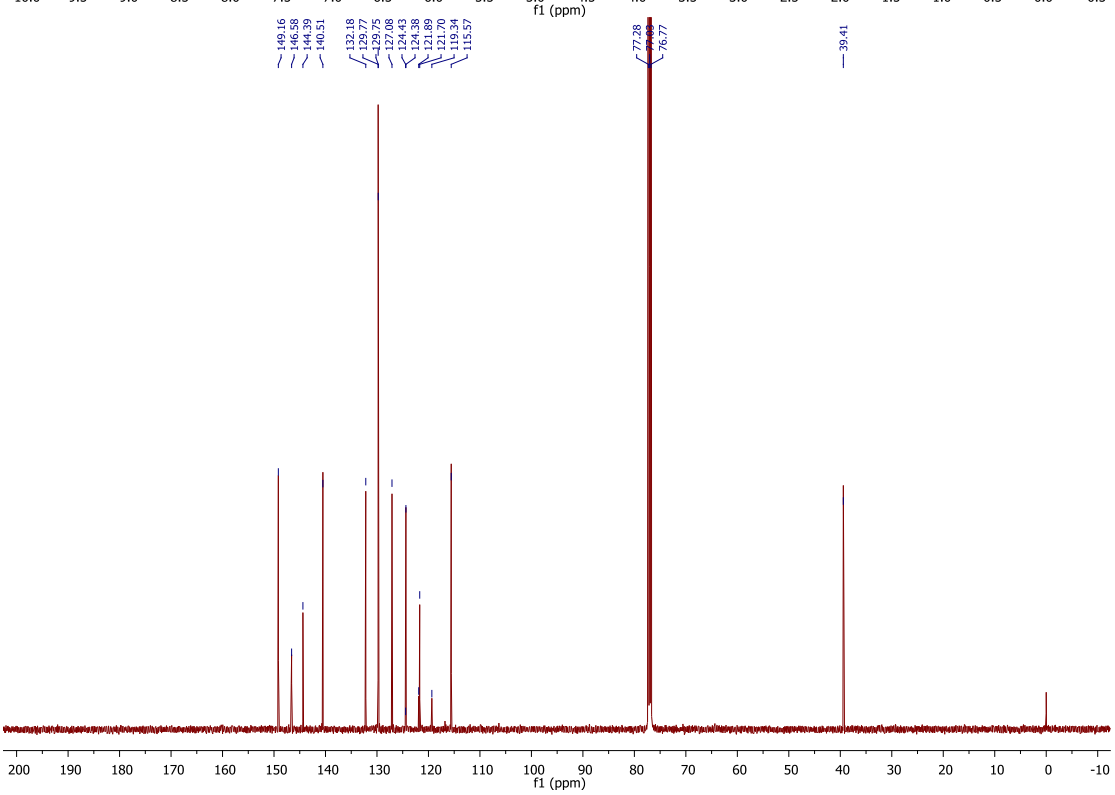

1.03
1.00
2.02
2.08
1.04
1.02
1.02
2.06
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

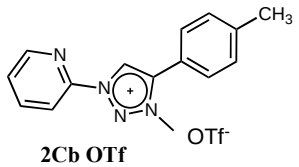

154.09
149.50
142.83
137.57
137.54
131.76
131.51
131.25
130.99
128.11
127.64
127.61
127.57
127.54
124.48
123.63
123.60
122.50
122.31
40.01
39.92
39.85
39.76
39.68
39.59
39.51
39.42
39.34
39.25
39.08
38.92
38.54
30.78
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
+
N
N
OTf-

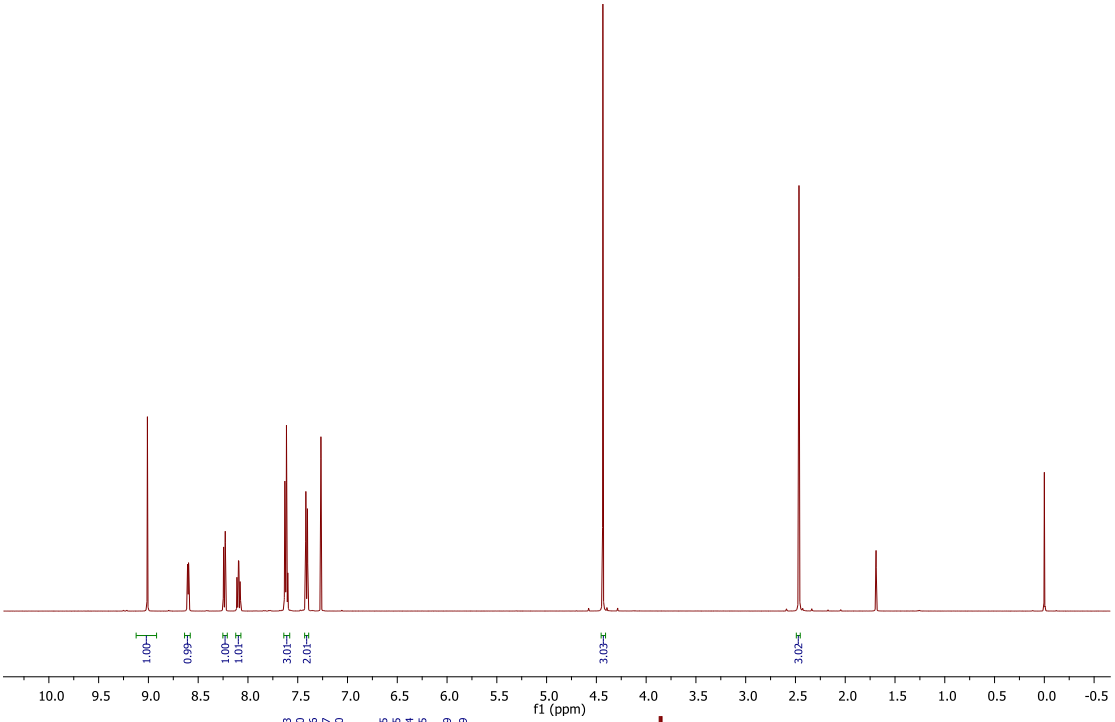
2Ca OTf

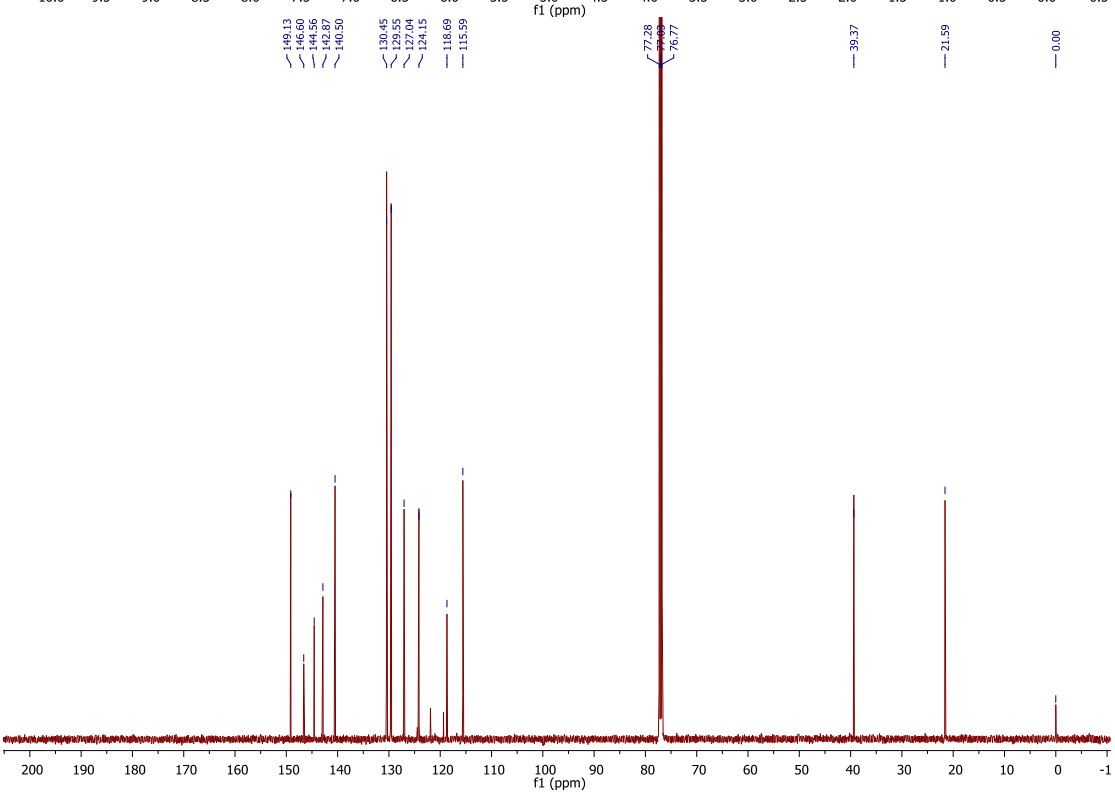

1.00
1.05
1.03
1.05
2.06
4.15
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

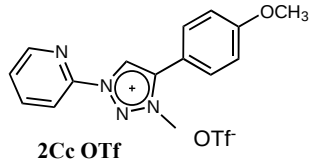

149.16
146.58
144.39
140.51
132.18
129.77
129.75
127.08
124.43
124.38
121.89
121.70
119.34
115.57
77.28
77.09
76.77
39.41
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CH3
N
N
N
N
+
OTf-

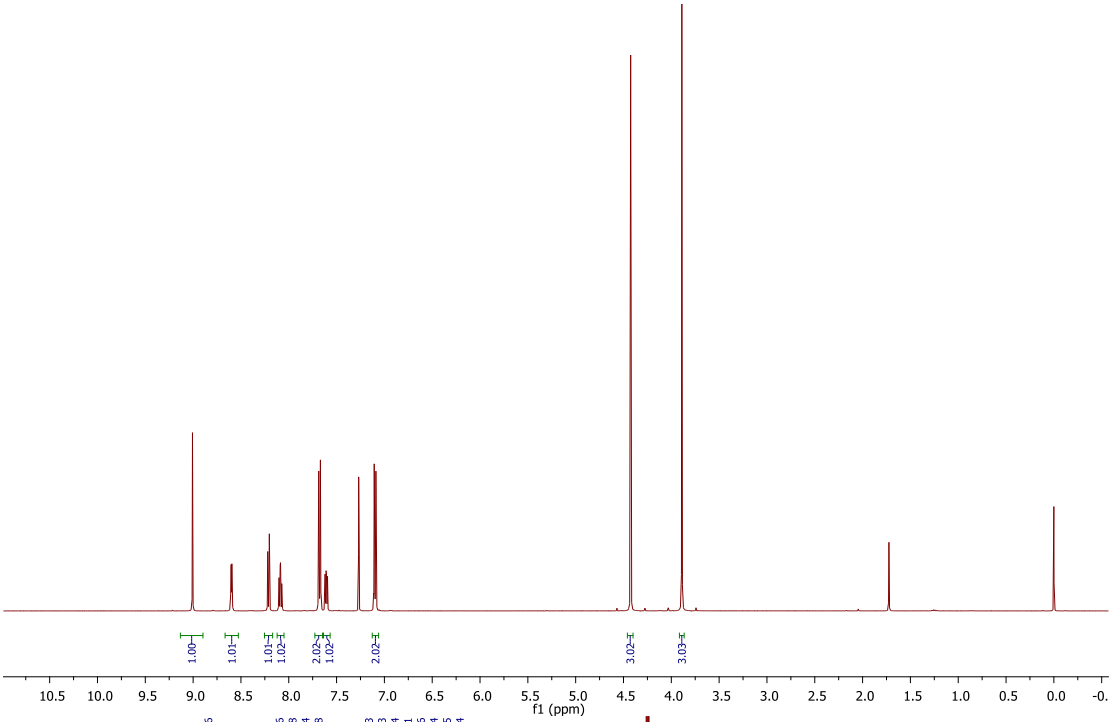
2Cb OTf

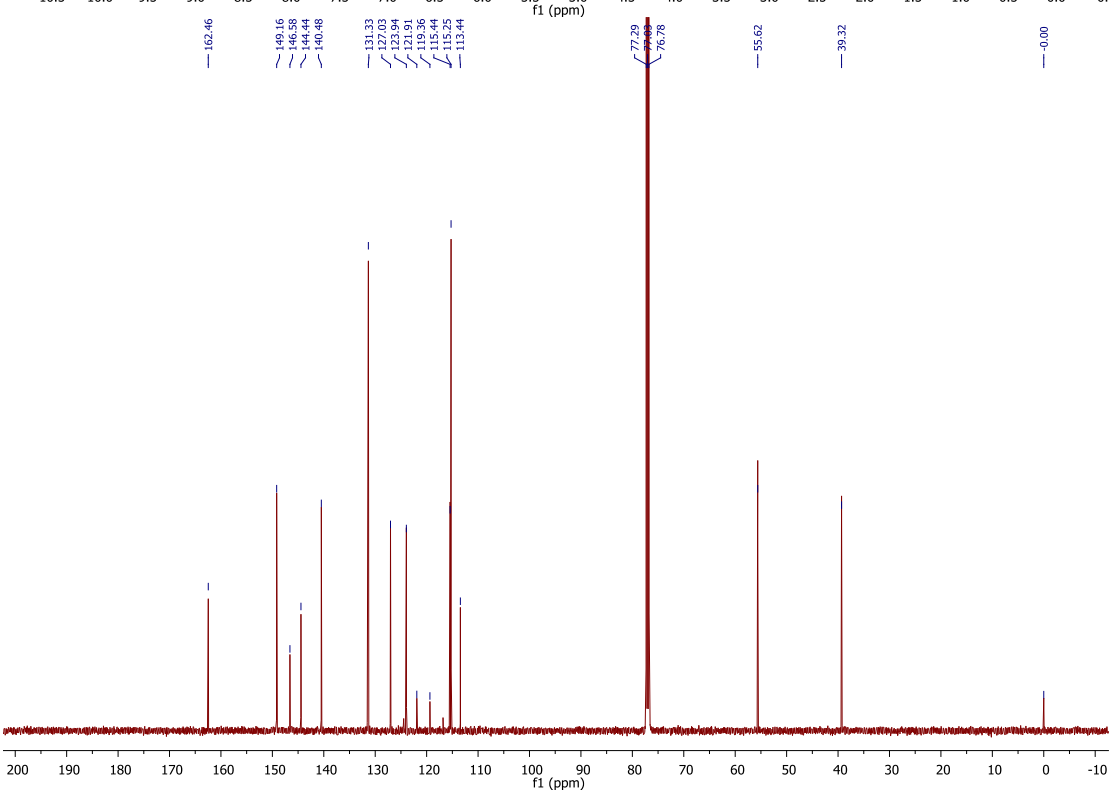

1.00
0.99
1.00
1.01
3.01
2.01
3.03
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

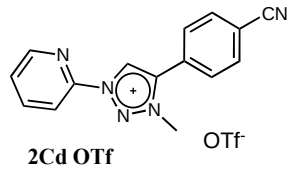

149.13
146.60
144.56
142.87
140.50
130.45
129.55
127.04
124.15
118.69
115.59
77.28
77.03
76.77
39.37
21.59
0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


OCH3
N
N
N
OTf-

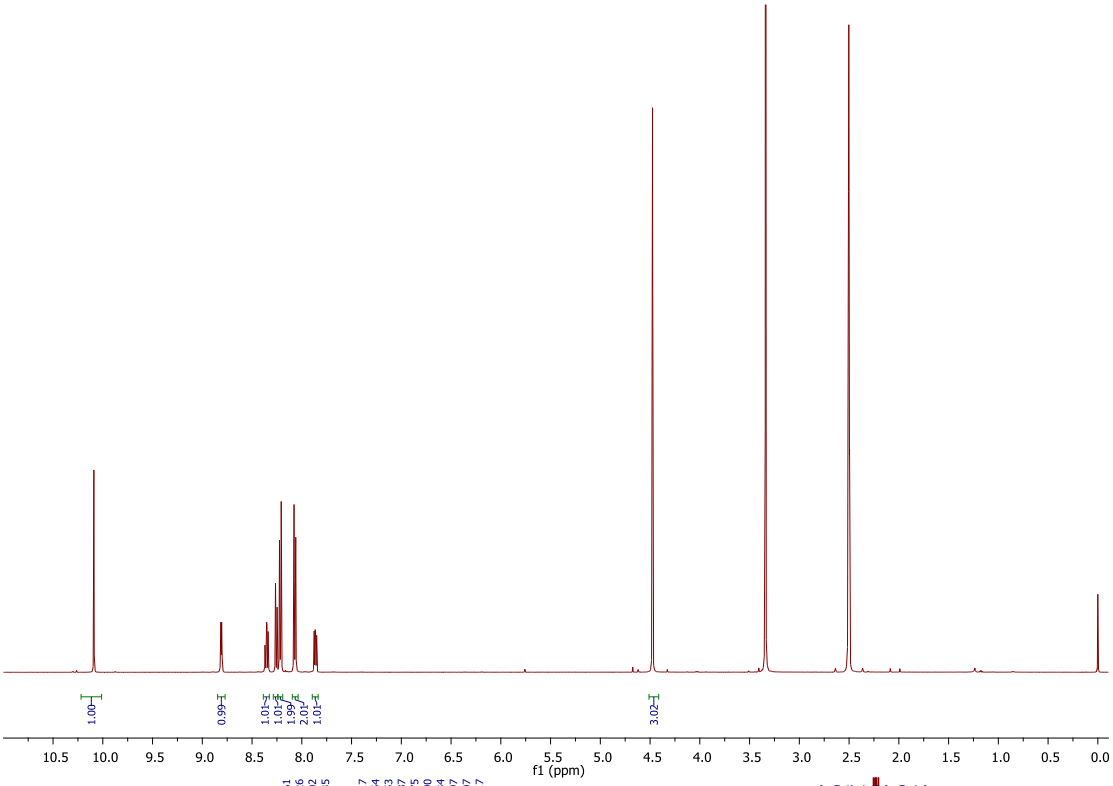
2Cc OTf

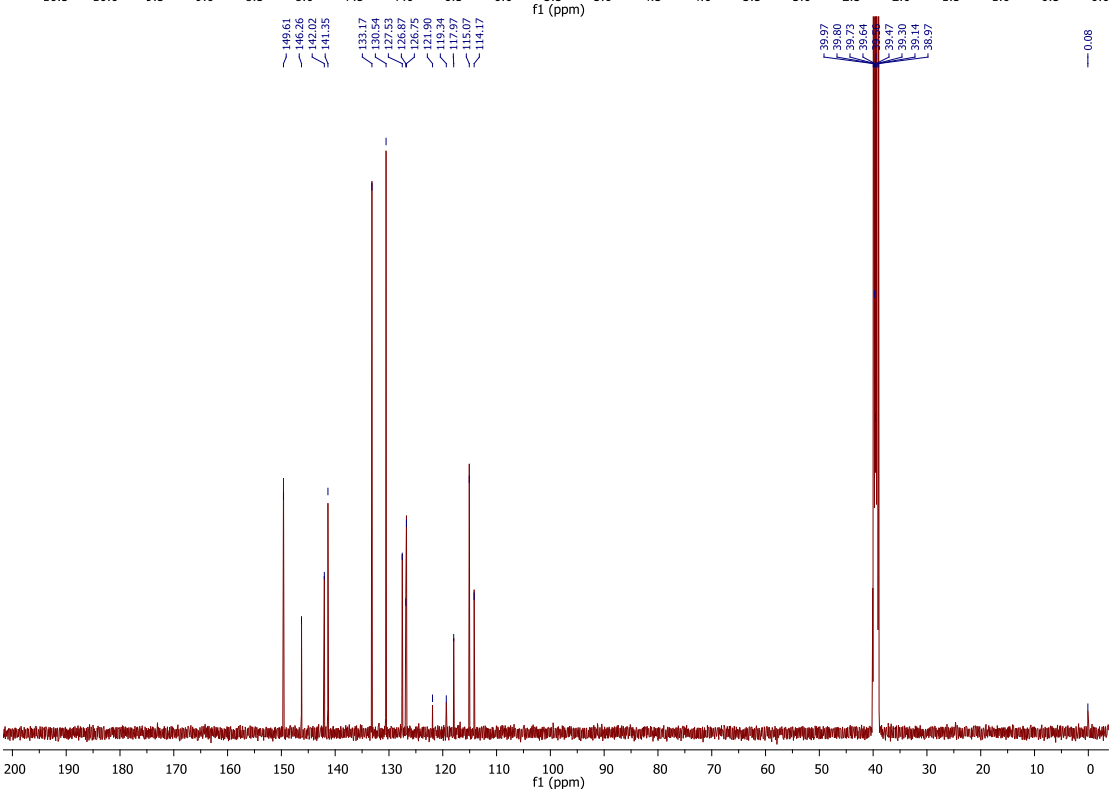

1.00
1.01
1.01
1.02
2.02
1.02
2.02
3.02
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

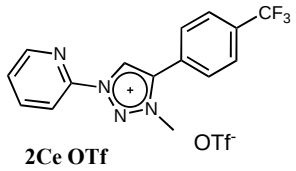

162.46
149.16
146.58
144.44
140.48
131.33
127.03
123.94
121.91
119.36
115.44
115.25
113.44
77.29
77.03
76.78
55.62
39.32
-0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CN
N
N
N
N
+
OTf-

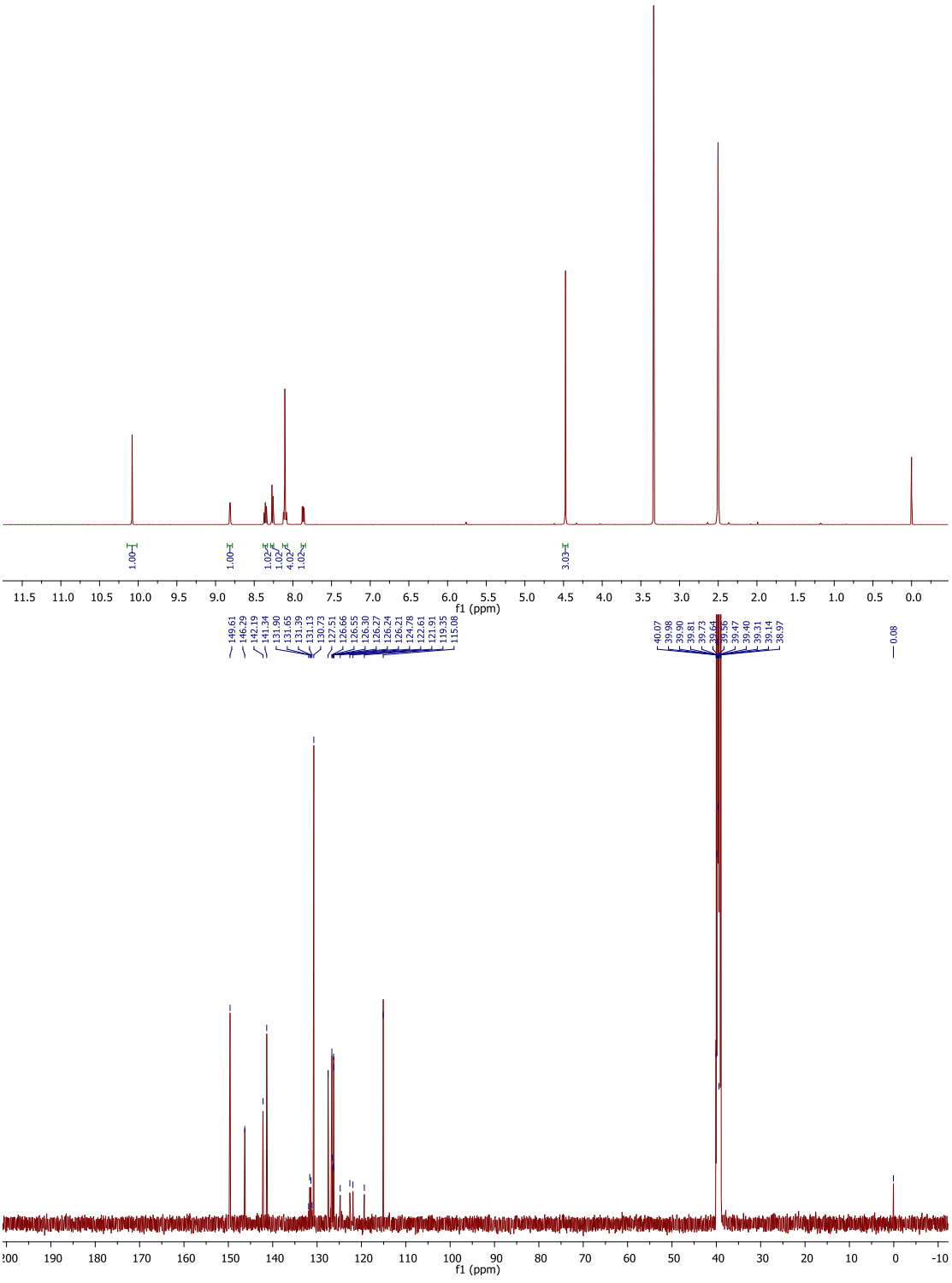
2Cd OTf

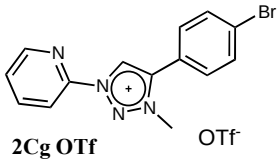

1.00
0.99
1.01
1.01
1.99
2.01
1.01
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.61
146.26
142.02
141.35
133.17
130.54
127.53
126.87
126.75
121.90
119.34
117.97
115.07
114.17
39.97
39.80
39.73
39.64
39.47
39.30
39.14
38.97
0.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

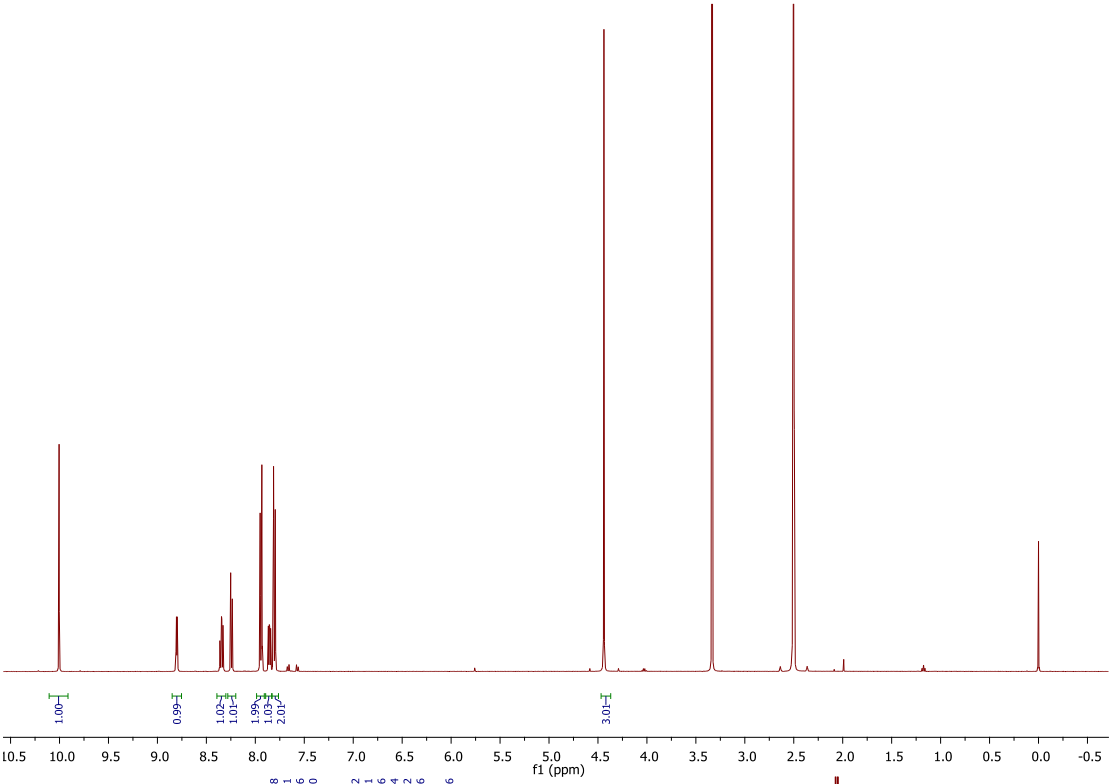

CF3
N
N
N
N
OTf-

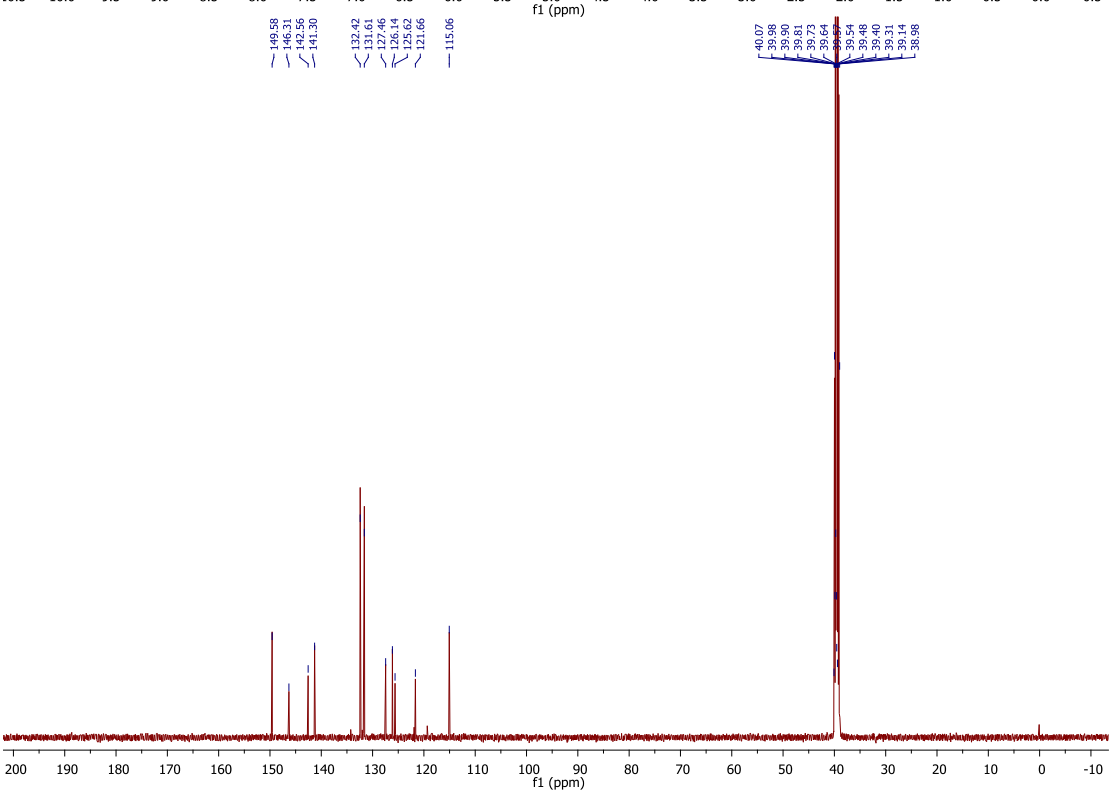
2Ce OTf

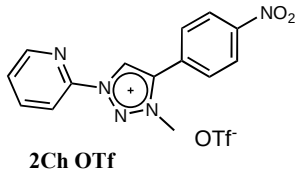

1.00
1.00
1.02
1.02
4.02
1.02
3.03
f1 (ppm)
149.61
146.29
142.19
141.34
131.90
131.65
131.39
131.13
130.73
127.51
126.66
126.55
126.39
126.27
126.24
126.21
124.78
122.61
121.91
119.35
115.08
40.07
39.98
39.90
39.81
39.73
39.64
39.55
39.47
39.40
39.31
39.14
38.97
0.08
f1 (ppm)


Br
N
N
N
N
+
OTf-

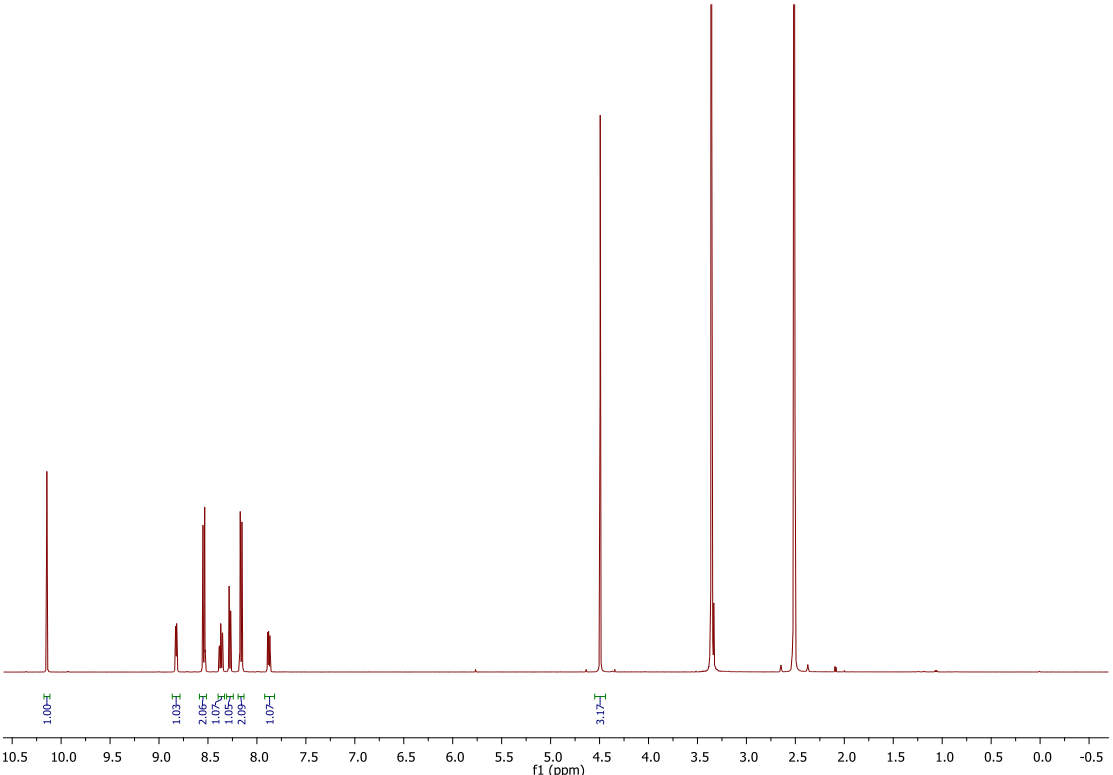
2Cg OTf

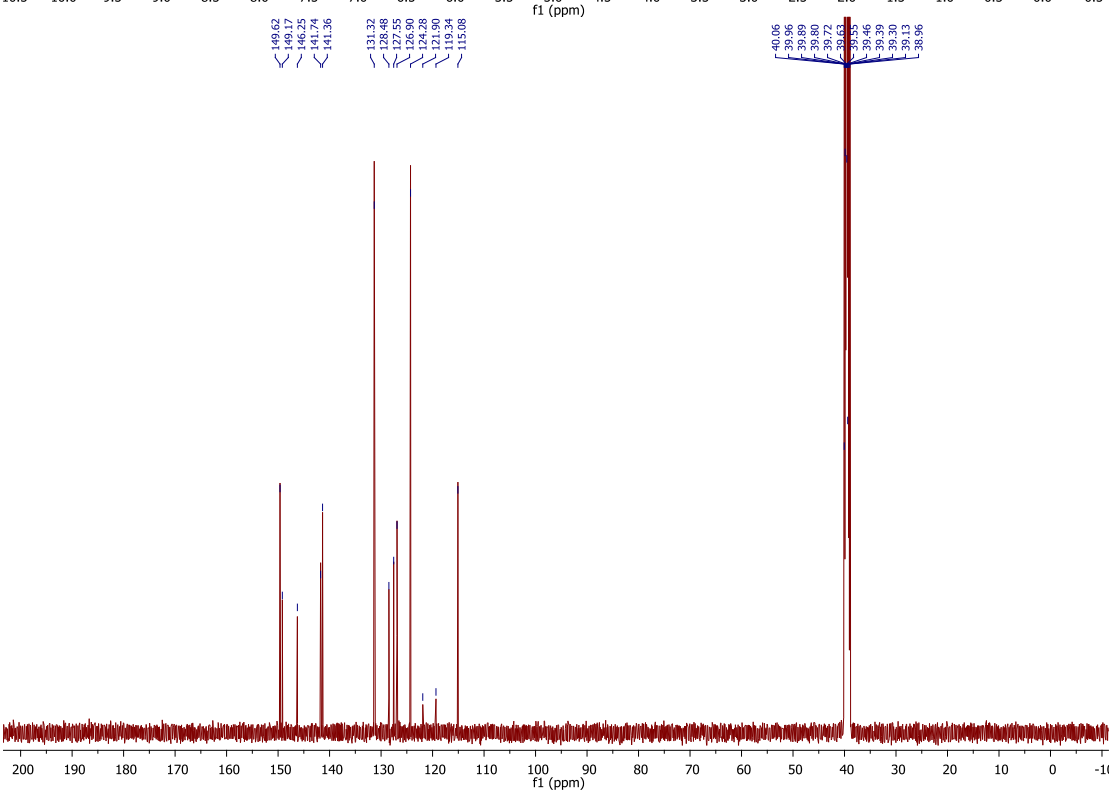

1.00
0.99
1.02
1.01
1.99
1.03
2.01
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

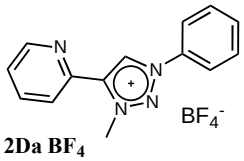

149.58
146.31
142.55
141.30
132.42
131.61
127.46
126.14
125.62
121.66
115.06
40.07
39.98
39.90
39.81
39.73
39.64
39.54
39.48
39.40
39.31
39.14
38.98
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NO2
N
N
N
N
OTf-

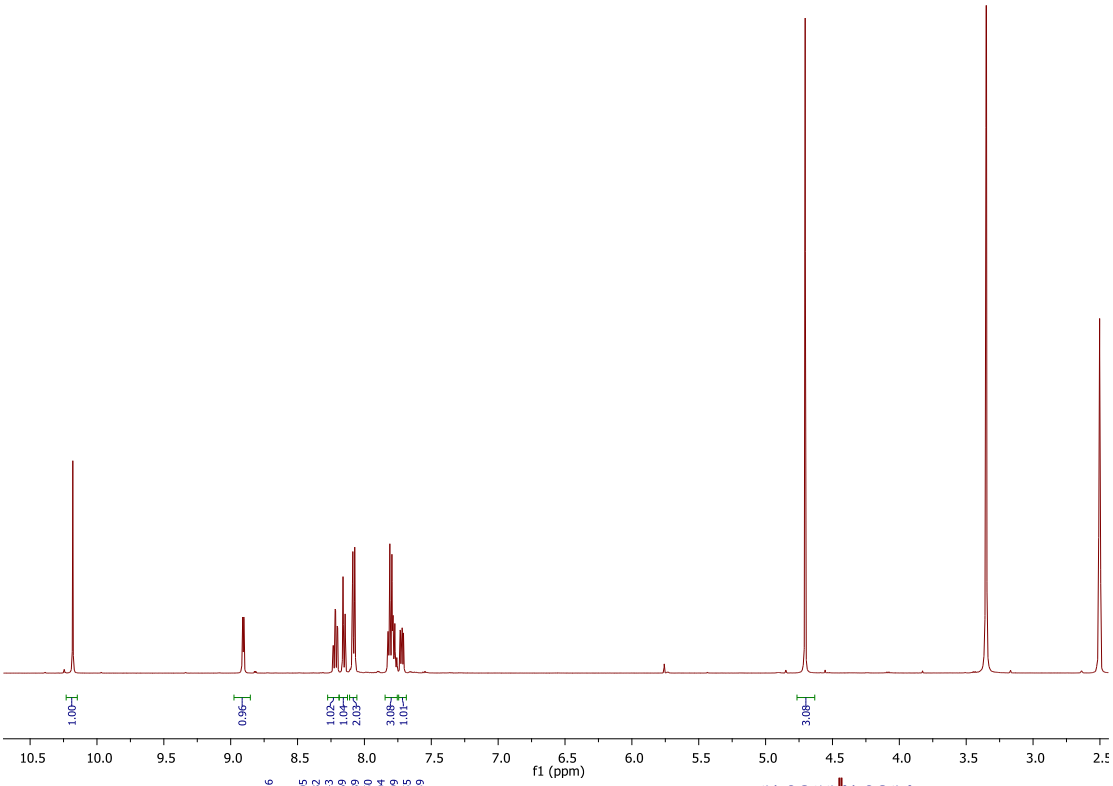
2Ch OTf

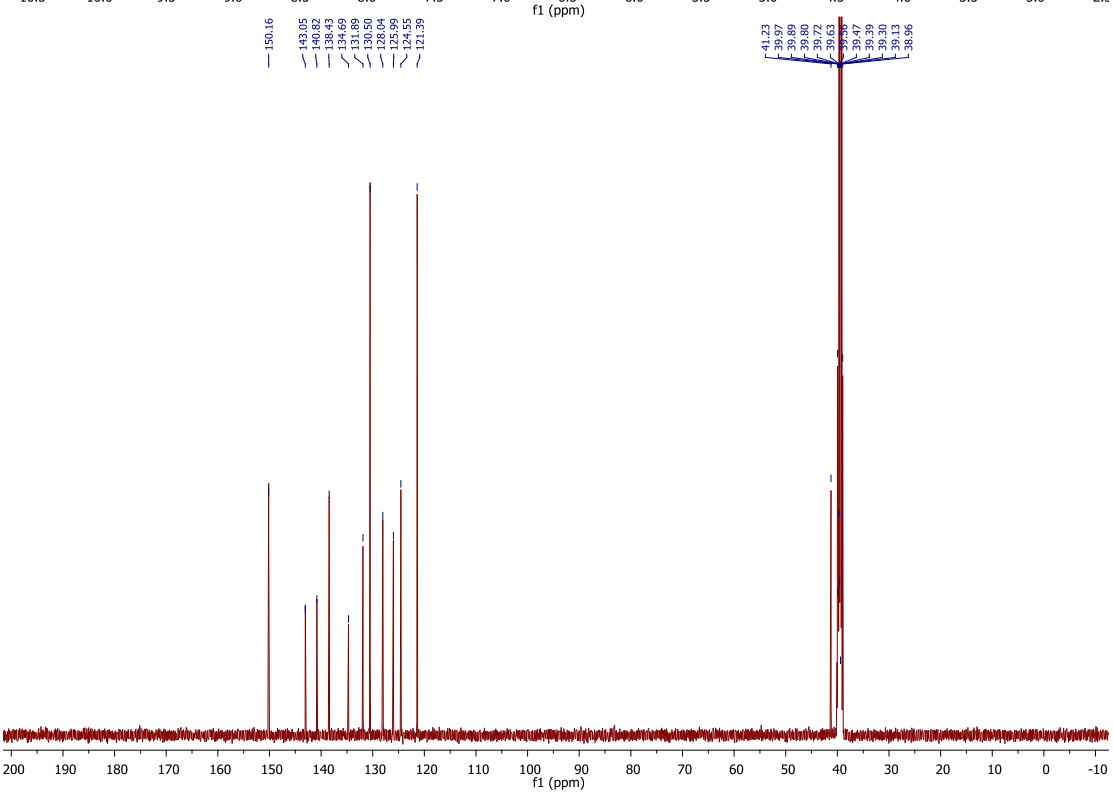

1.00
1.03
2.06
1.07
1.05
2.09
1.07
3.17
f1 (ppm)

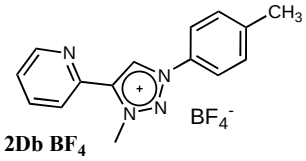

149.62
149.17
146.25
144.74
141.36
131.32
128.48
127.55
126.90
124.28
121.90
119.34
115.08
40.06
39.96
39.89
39.80
39.72
39.63
39.55
39.46
39.39
39.30
39.13
38.96
f1 (ppm)


N
N
N
N
BF4-

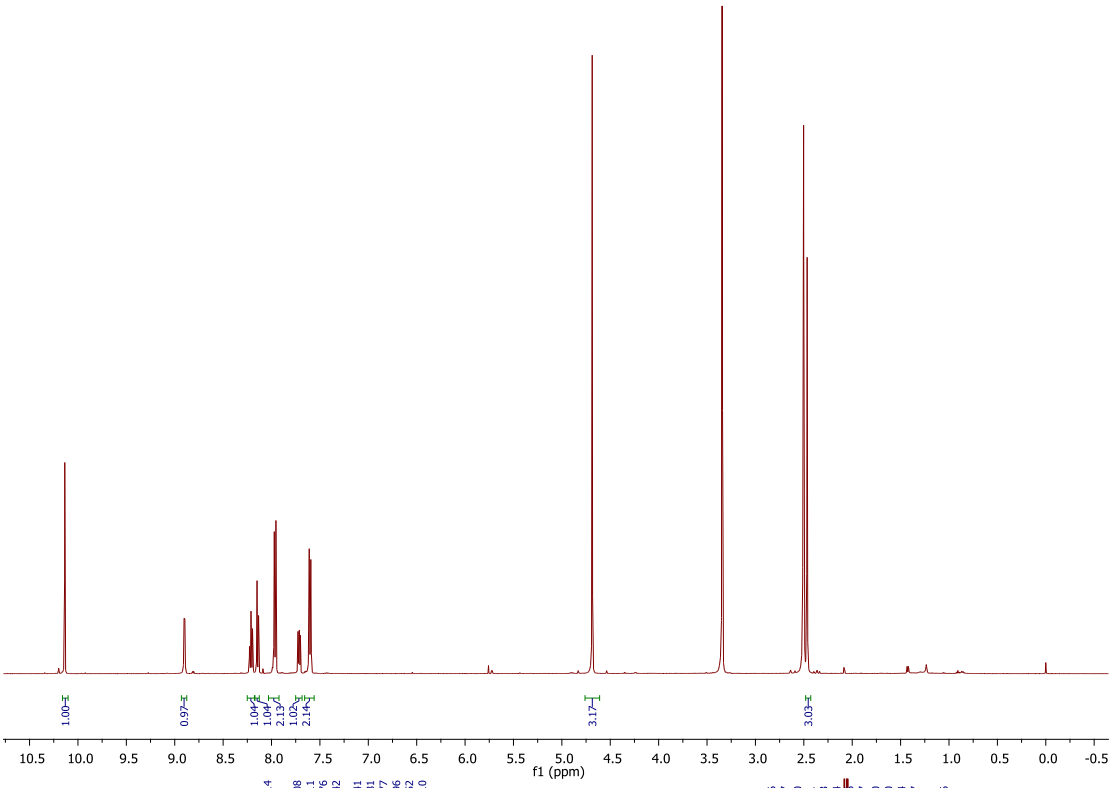
2Da BF_4

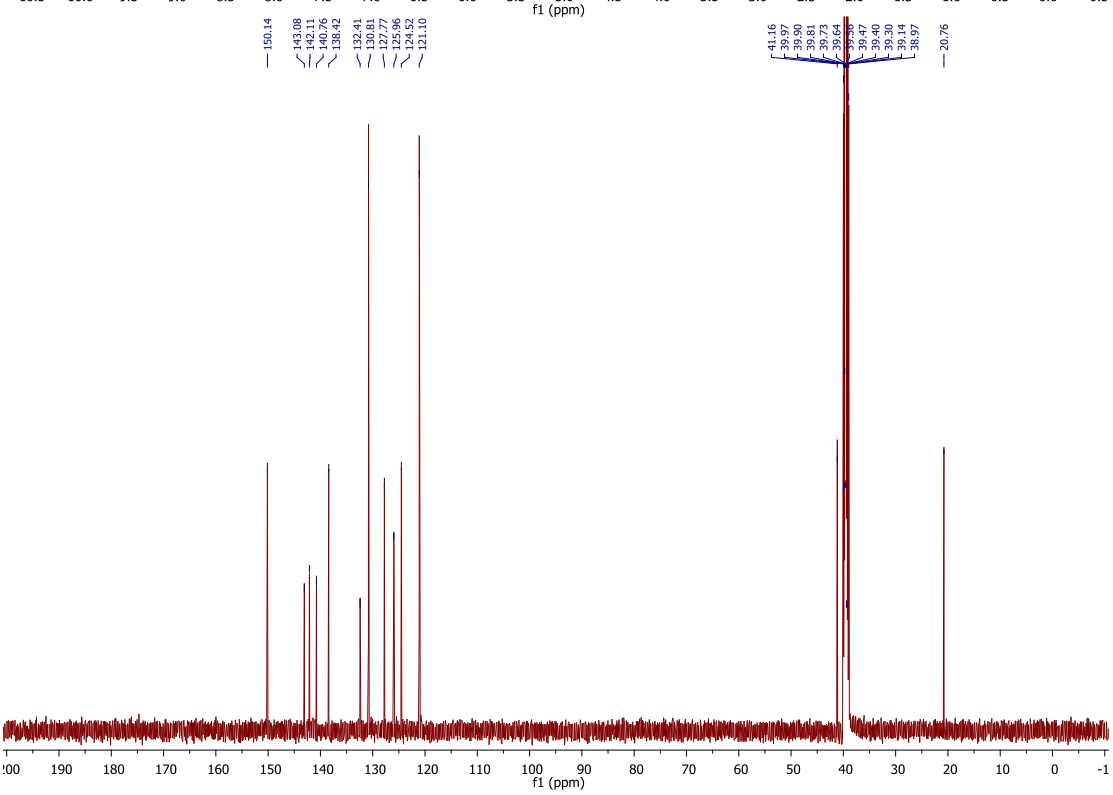

1.00
0.96
1.02
1.04
2.03
3.09
1.01
3.08
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

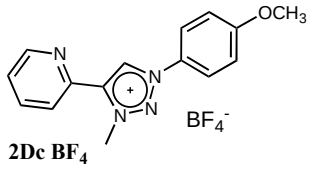

150.16
143.05
140.82
138.43
134.69
131.89
130.50
128.04
125.99
124.55
121.39
41.23
39.97
39.89
39.80
39.72
39.63
39.56
39.47
39.39
39.30
39.13
38.96
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CH3
N
N
N
N
+
BF4-

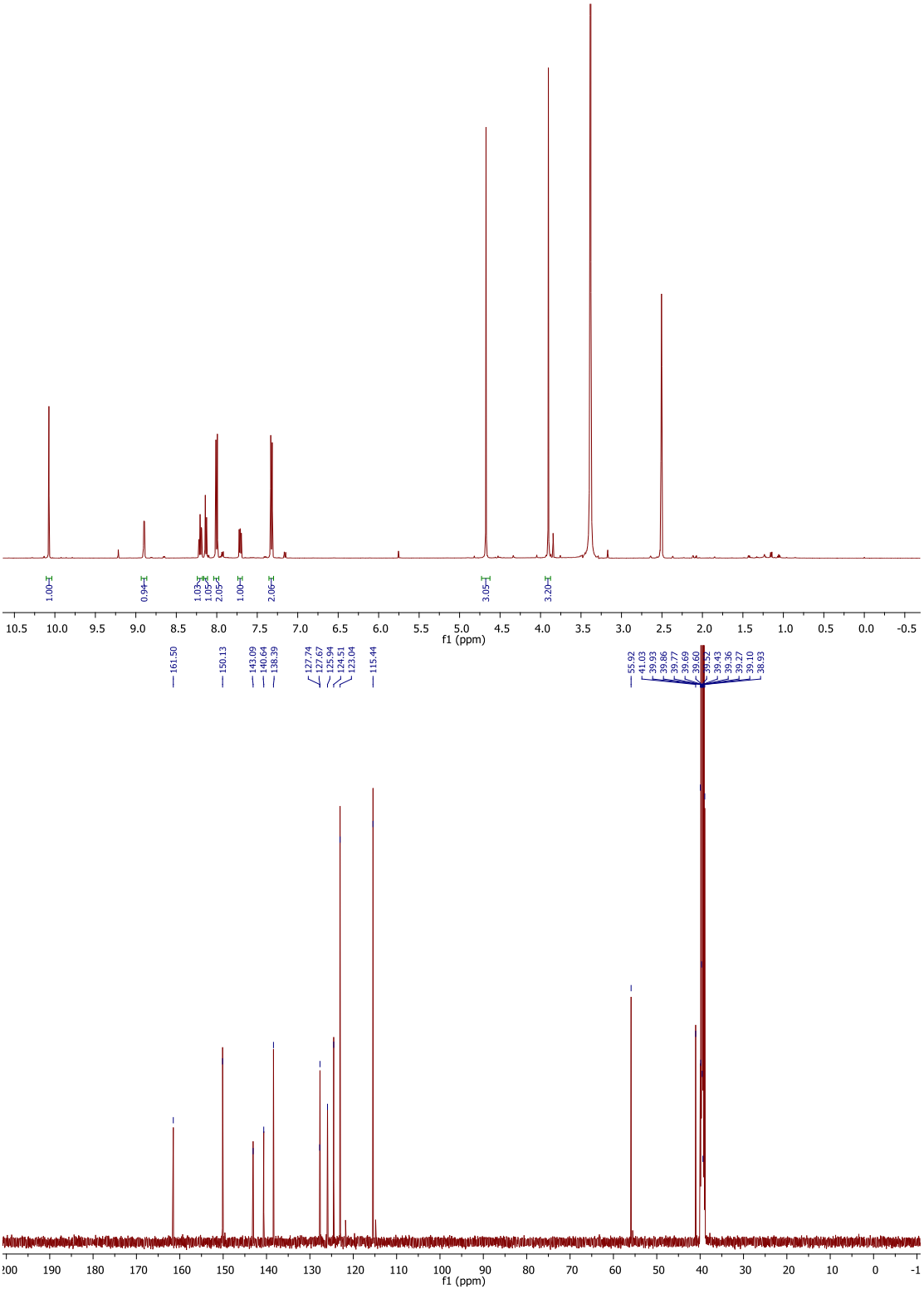
2Db BF_4

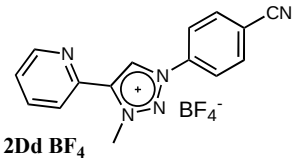

1.00
0.97
1.04
1.04
2.13
1.02
2.14
3.17
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


150.14
143.08
142.11
140.76
138.42
132.41
130.81
127.77
125.96
124.52
121.10
41.16
39.97
39.90
39.81
39.73
39.64
39.47
39.40
39.30
39.14
38.97
20.76
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

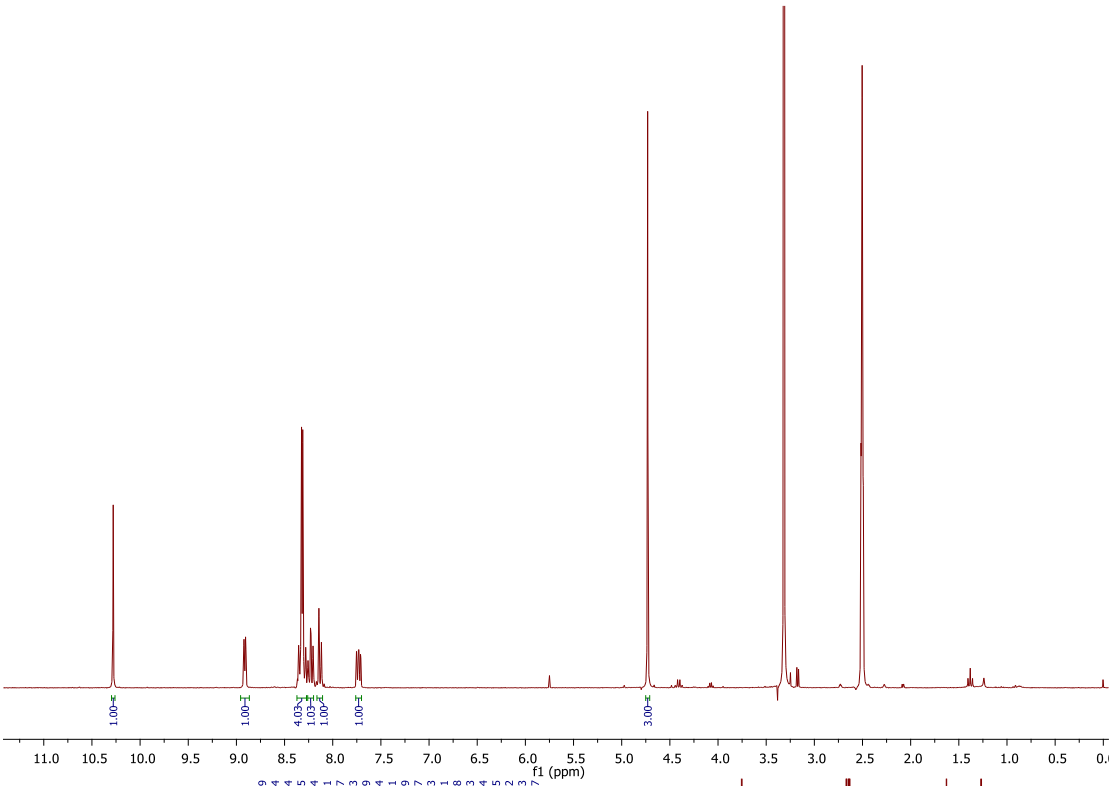

OCH3
N
N
N
N
BF4-

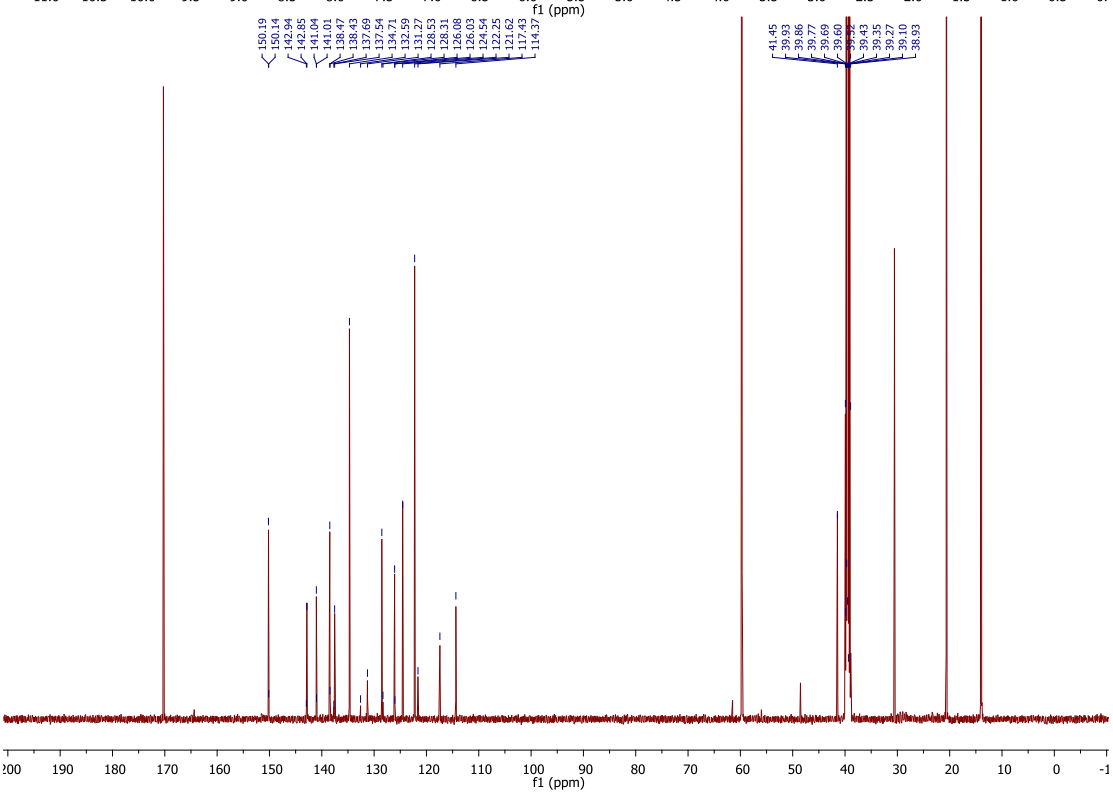
2Dc BF_4

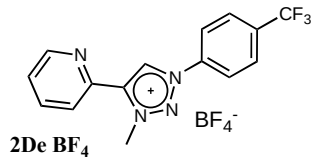

1.00
0.94
1.03
1.05
2.05
1.00
2.06
3.05
3.20
f1 (ppm)
161.50
150.13
143.09
140.64
138.39
127.74
127.67
125.94
124.51
123.04
115.44
55.92
41.03
39.93
39.86
39.77
39.69
39.60
39.52
39.43
39.36
39.27
39.10
38.93
f1 (ppm)


CN
N
N
N
N
BF4-

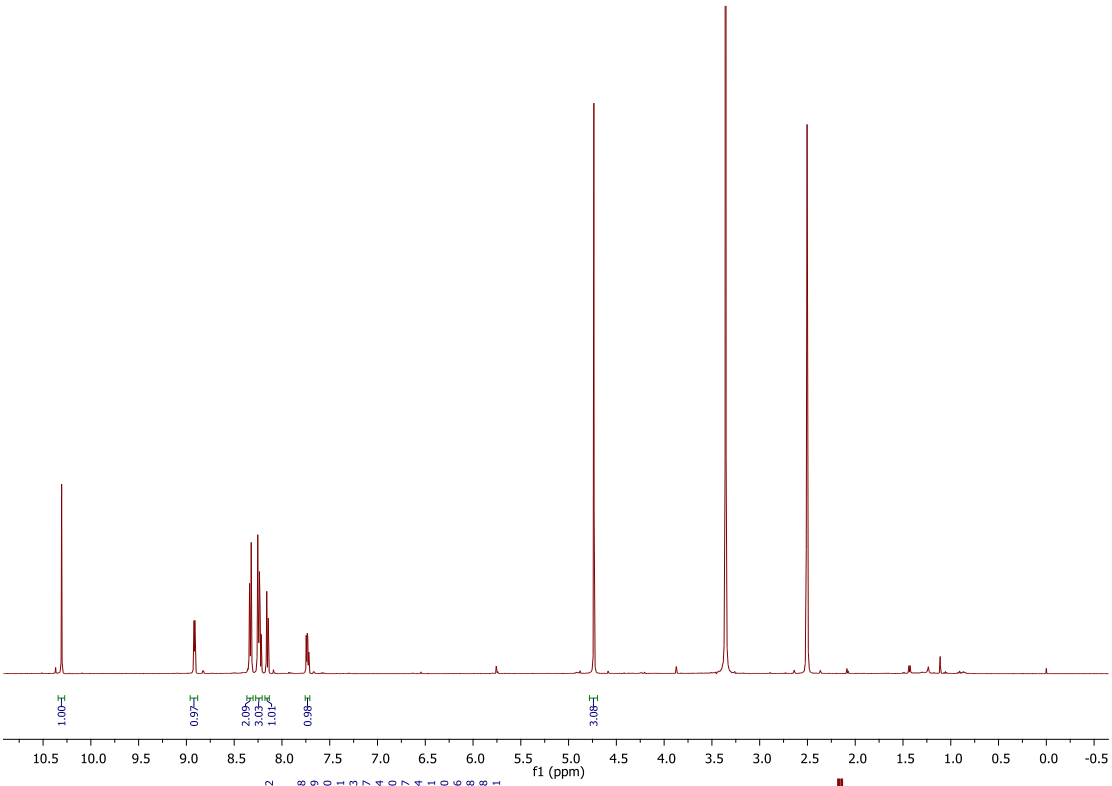
2Dd BF_4

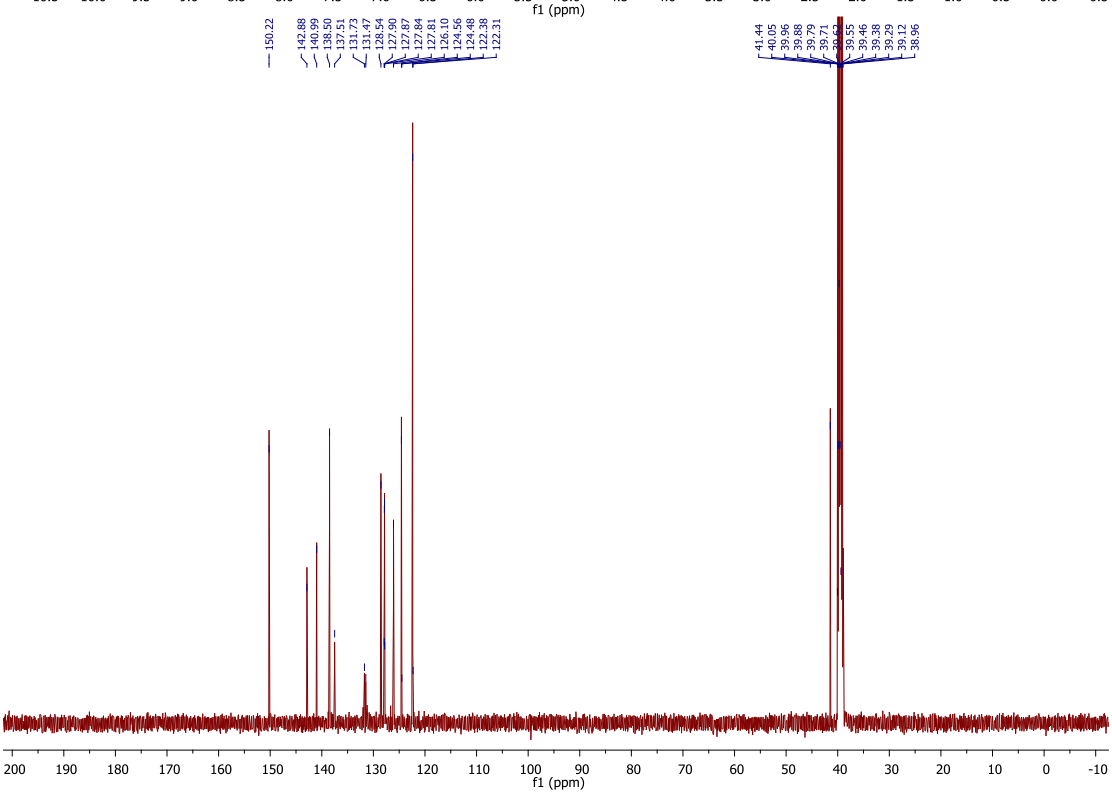

1.00
1.00
4.03
1.03
1.00
1.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

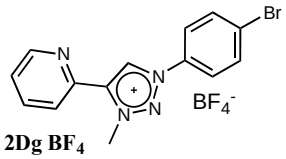

150.19
150.14
142.94
142.85
141.04
141.01
138.47
138.43
137.69
137.54
134.71
132.59
131.27
128.53
128.31
126.08
126.03
124.54
122.25
121.62
117.43
114.37
41.45
39.93
39.86
39.77
39.69
39.60
39.52
39.43
39.35
39.27
39.10
38.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


CF3
N
N
N
N
BF4-

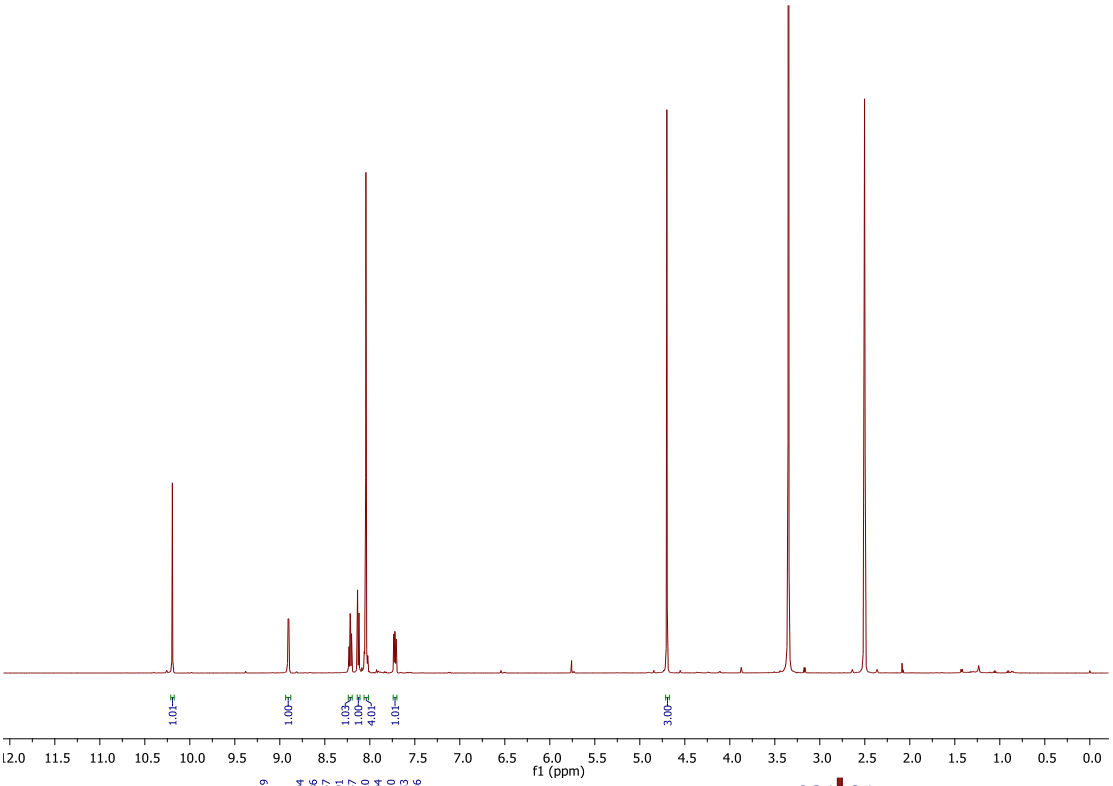
2De BF_4

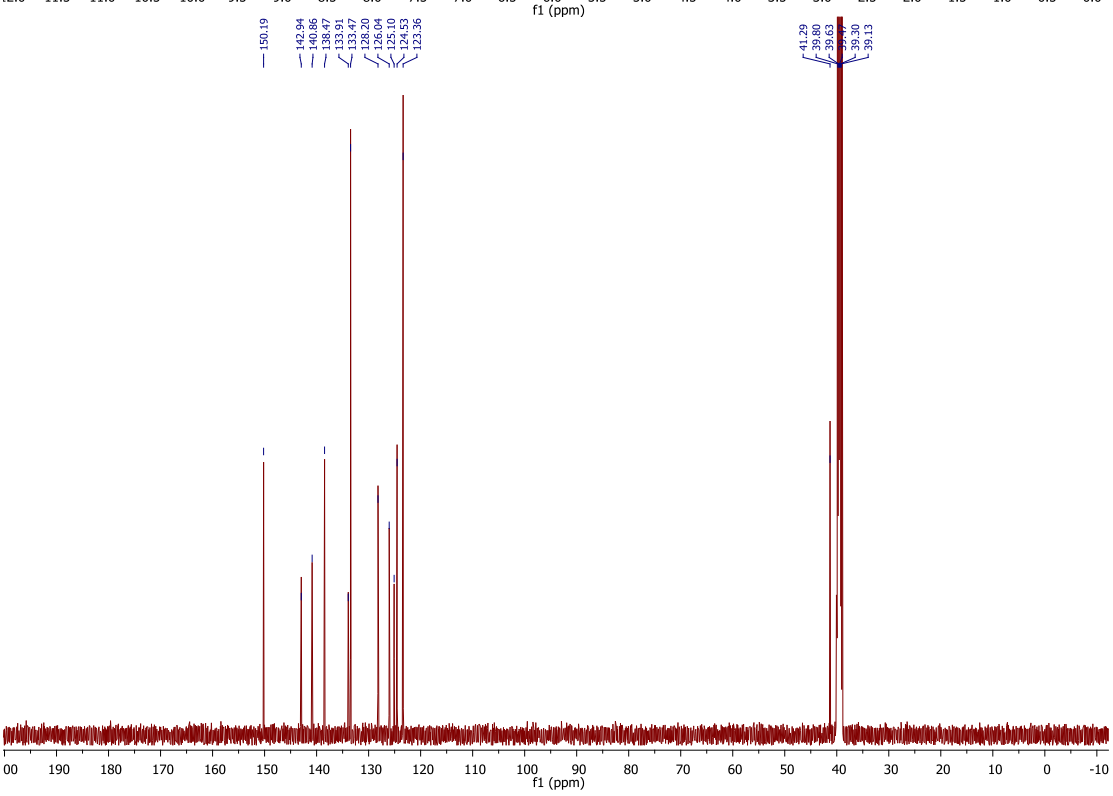

1.00
0.97
2.09
3.05
1.01
0.98
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

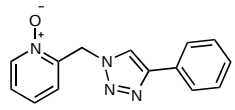

150.22
142.88
140.99
138.50
137.51
131.73
131.47
128.54
127.90
127.87
127.84
127.81
126.10
124.56
124.48
122.38
122.31
41.44
40.05
39.96
39.88
39.79
39.71
39.62
39.55
39.46
39.38
39.29
39.21
38.96
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Br
N
N
N
N
+
BF4-

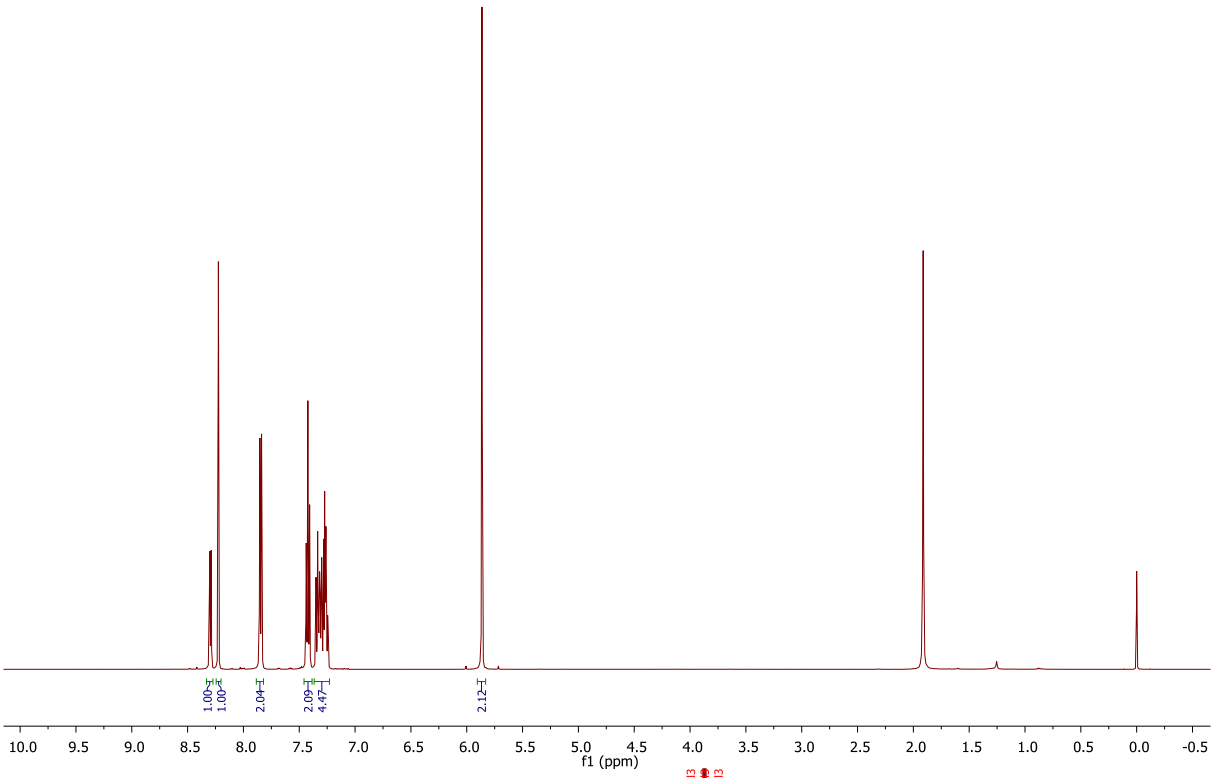
2Dg BF_4

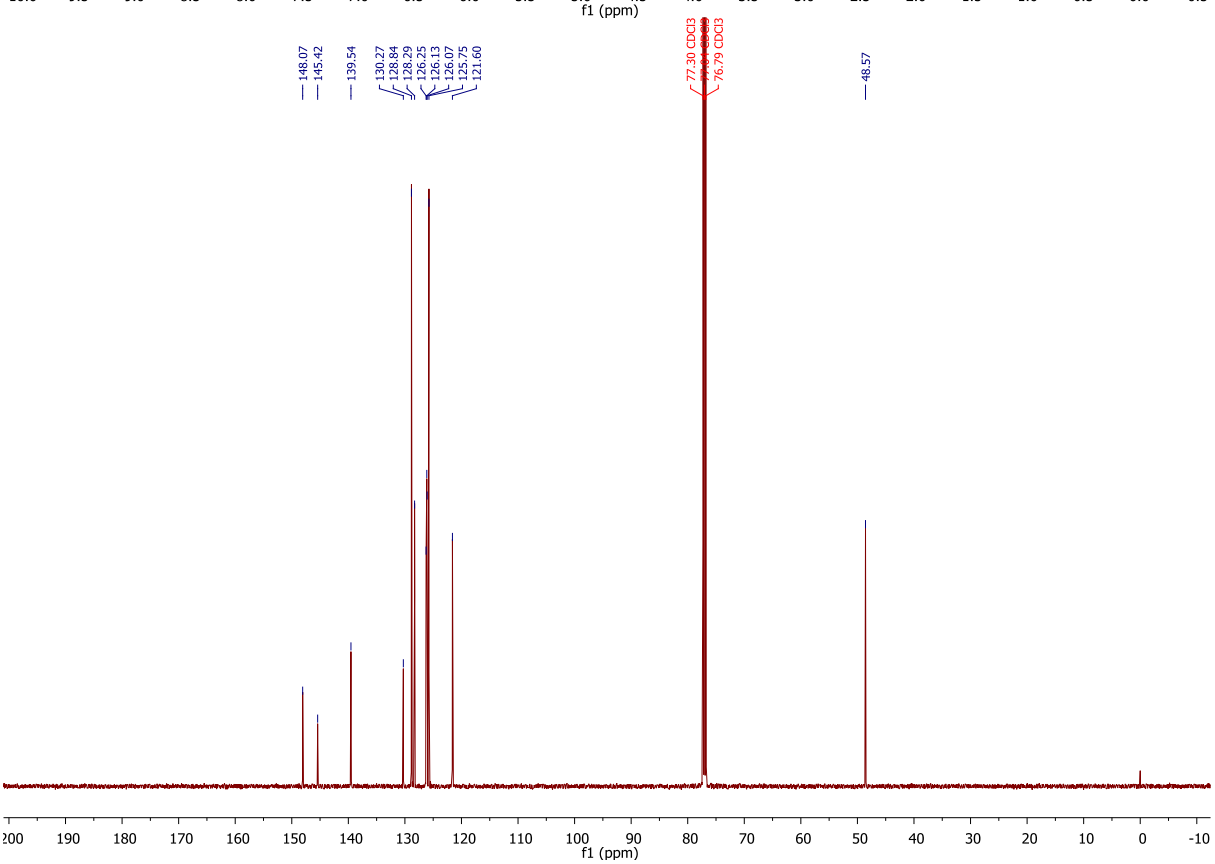

1.01
1.00
1.03
1.00
4.01
1.01
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

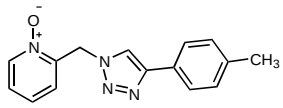

150.19
142.94
140.86
138.47
133.91
133.47
128.20
126.04
125.10
124.53
123.36
41.29
39.80
39.63
39.47
39.30
39.13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



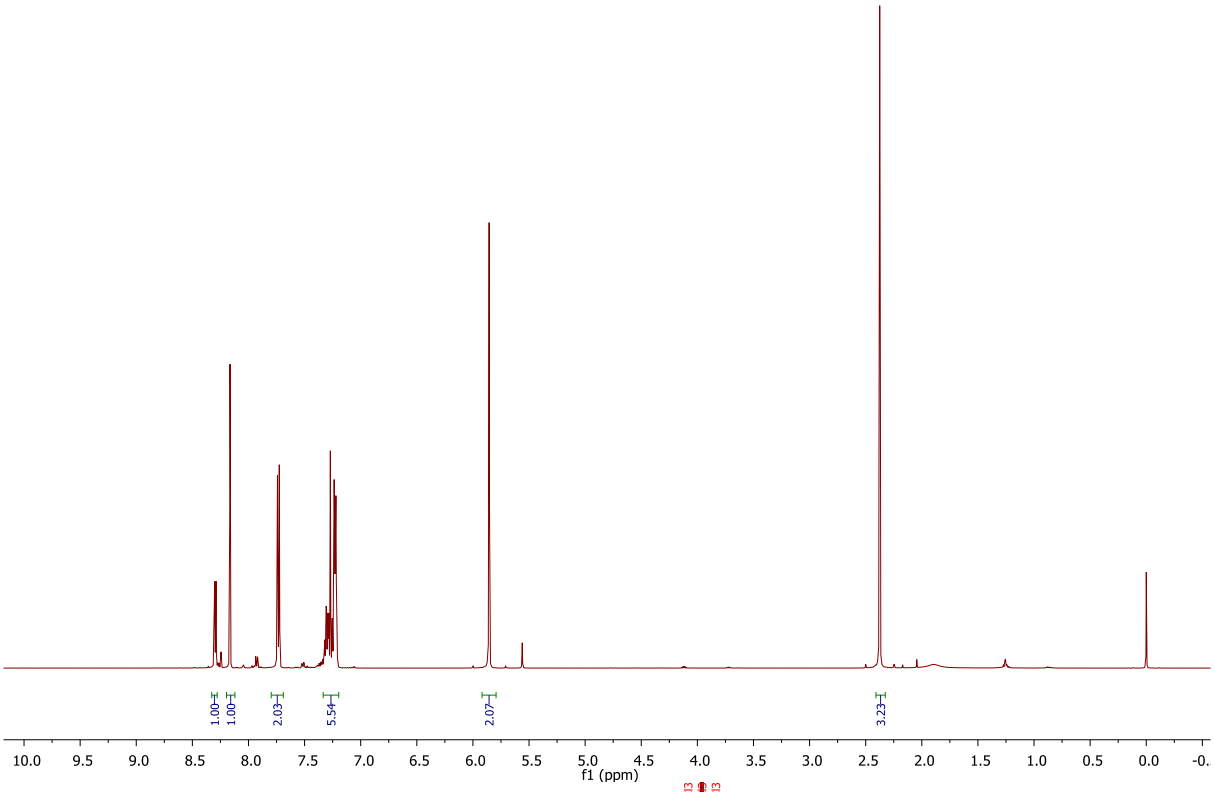
3Aa

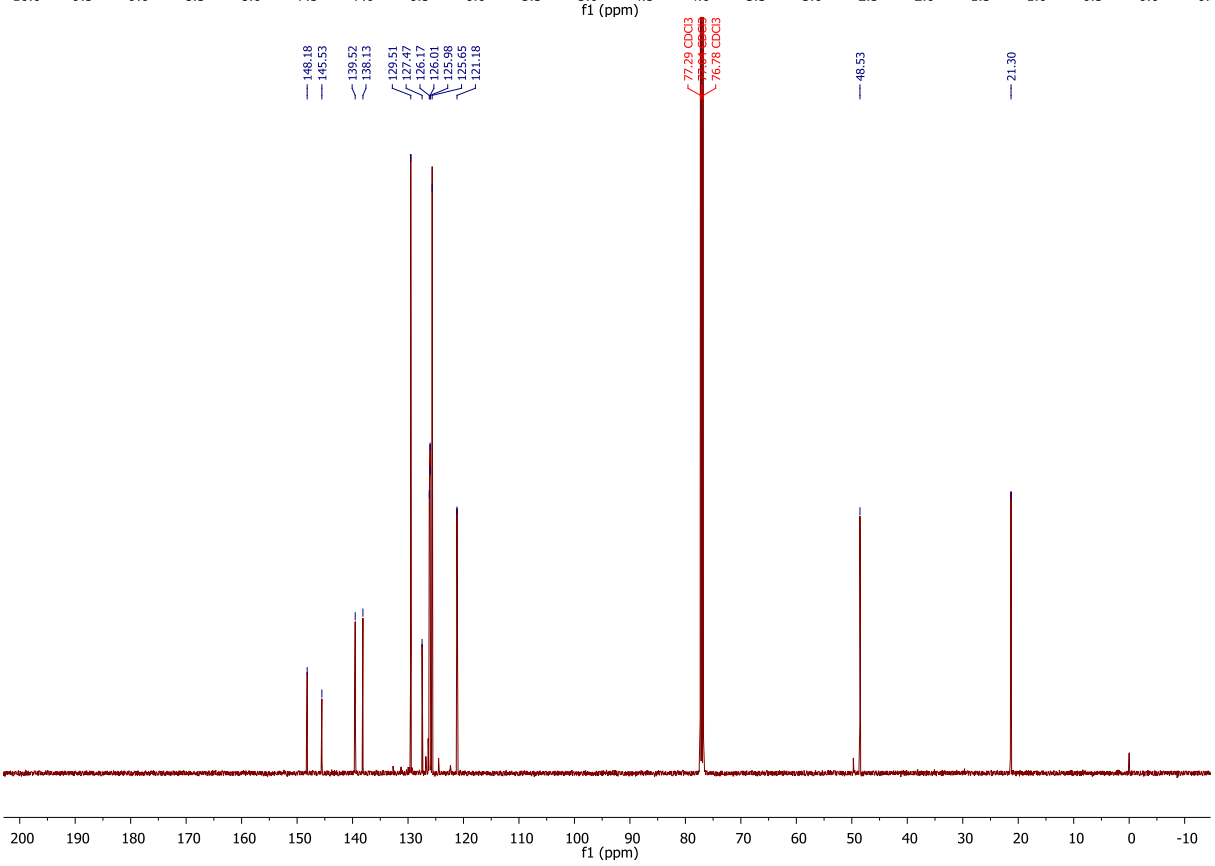

1.00
1.00
2.04
2.09
4.47
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

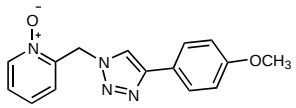

148.07
145.42
139.54
130.27
128.84
128.29
126.25
126.13
126.07
125.75
121.60
77.30 CDCl3
76.79 CDCl3
48.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



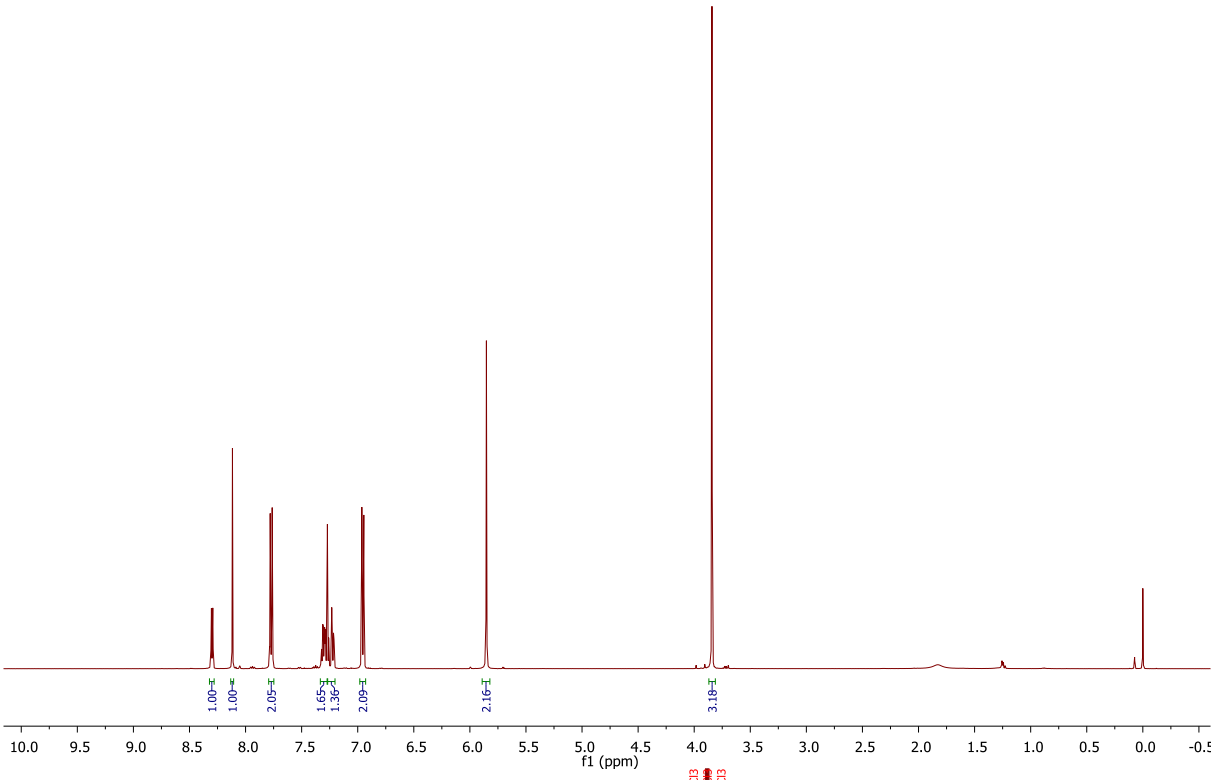
3Ab

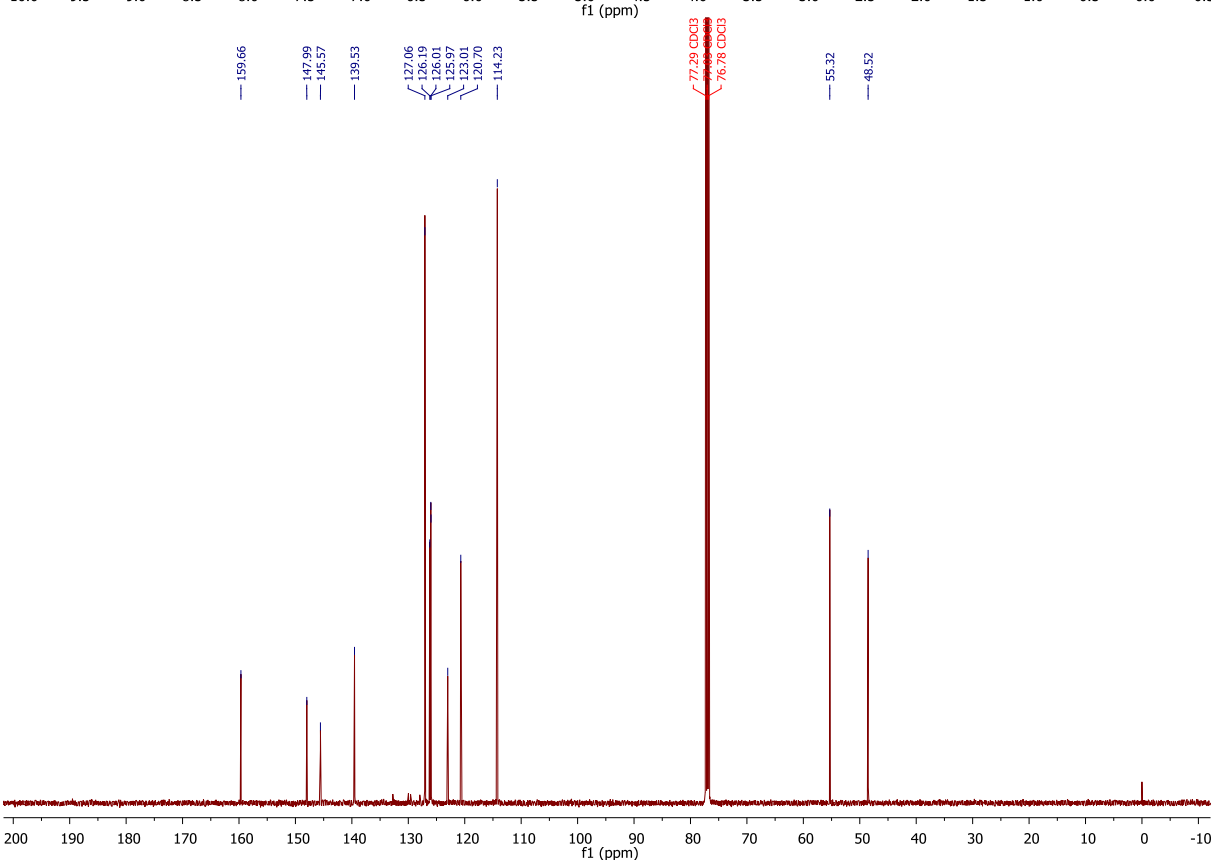

1.00
1.00
2.03
5.54
2.07
3.23
f1 (ppm)

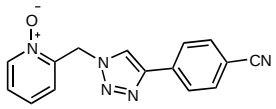

148.18
145.53
139.52
138.13
129.51
127.47
126.17
126.01
125.98
125.65
121.18
77.29 CDCl3
76.78 CDCl3
48.53
21.30
f1 (ppm)


O
N+
N
N=N
OCH3

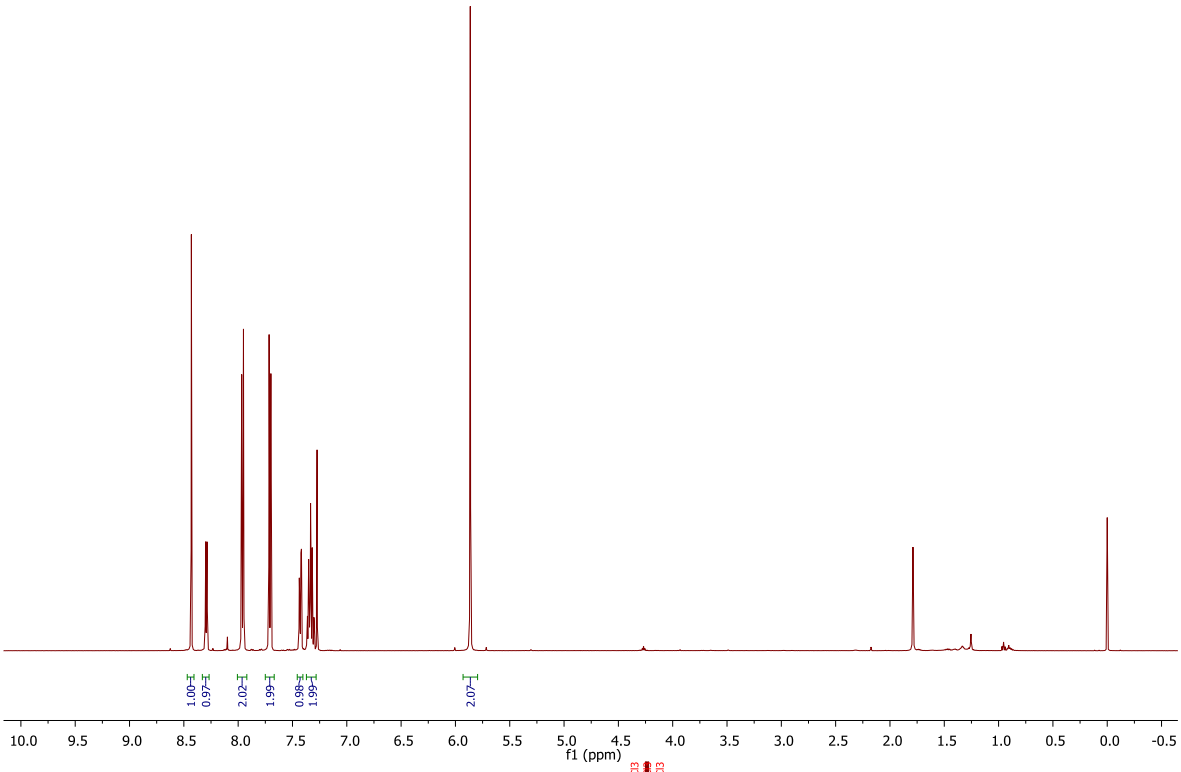
3Ac

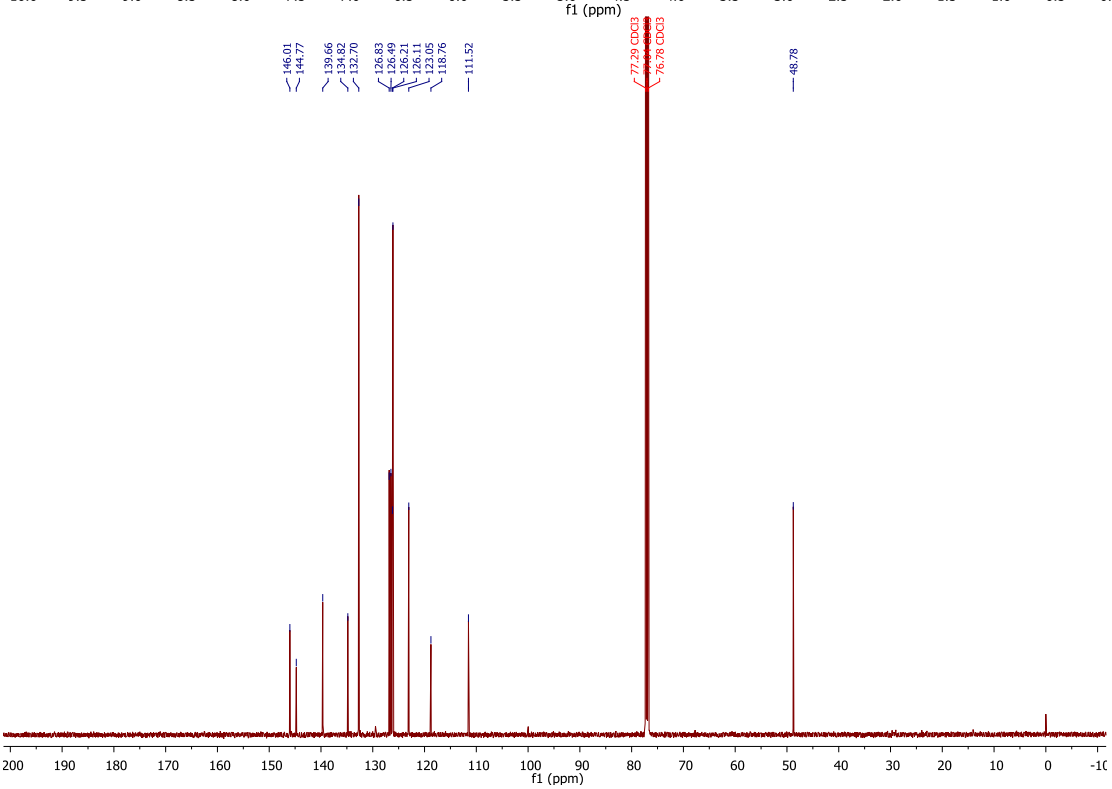

1.00
1.00
2.05
1.65
1.36
2.09
2.16
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

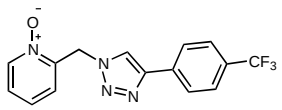

159.66
147.99
145.57
139.53
127.06
126.19
126.01
125.97
123.01
120.70
114.23
77.29 CDCl3
76.78 CDCl3
55.32
48.52
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
N
N
N
N
CN

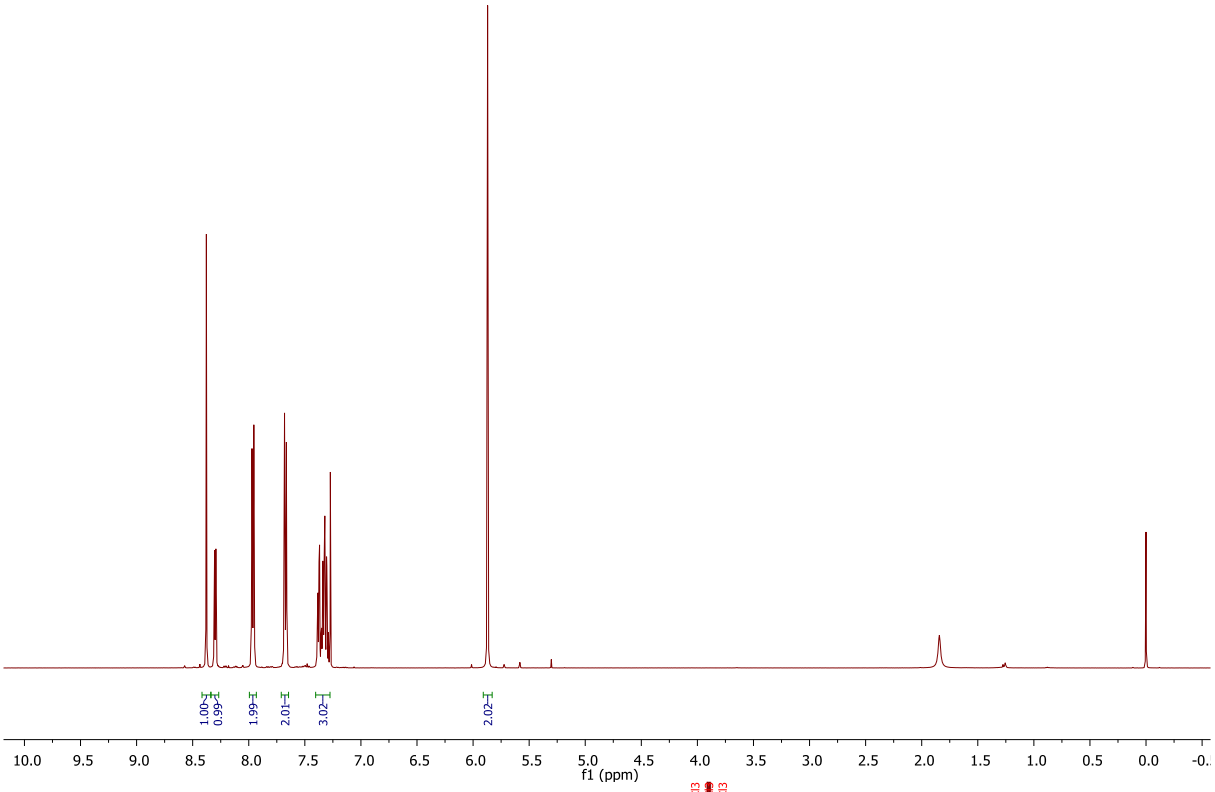
3Ad

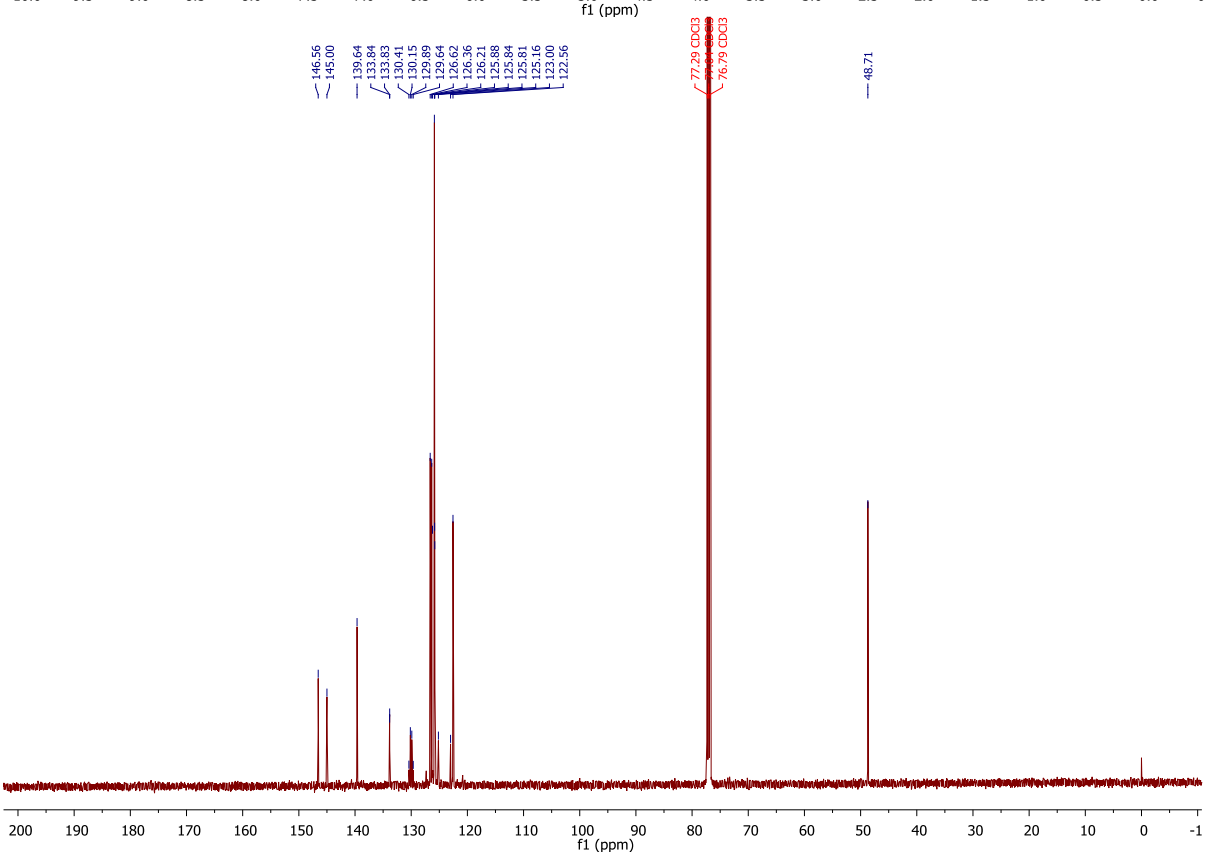

1.00
0.97
2.02
1.99
0.98
1.99
2.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

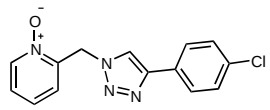

146.01
144.77
139.66
134.82
132.70
126.83
126.49
126.21
126.11
123.05
118.76
111.52
77.29 CDCl3
76.78 CDCl3
48.78
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



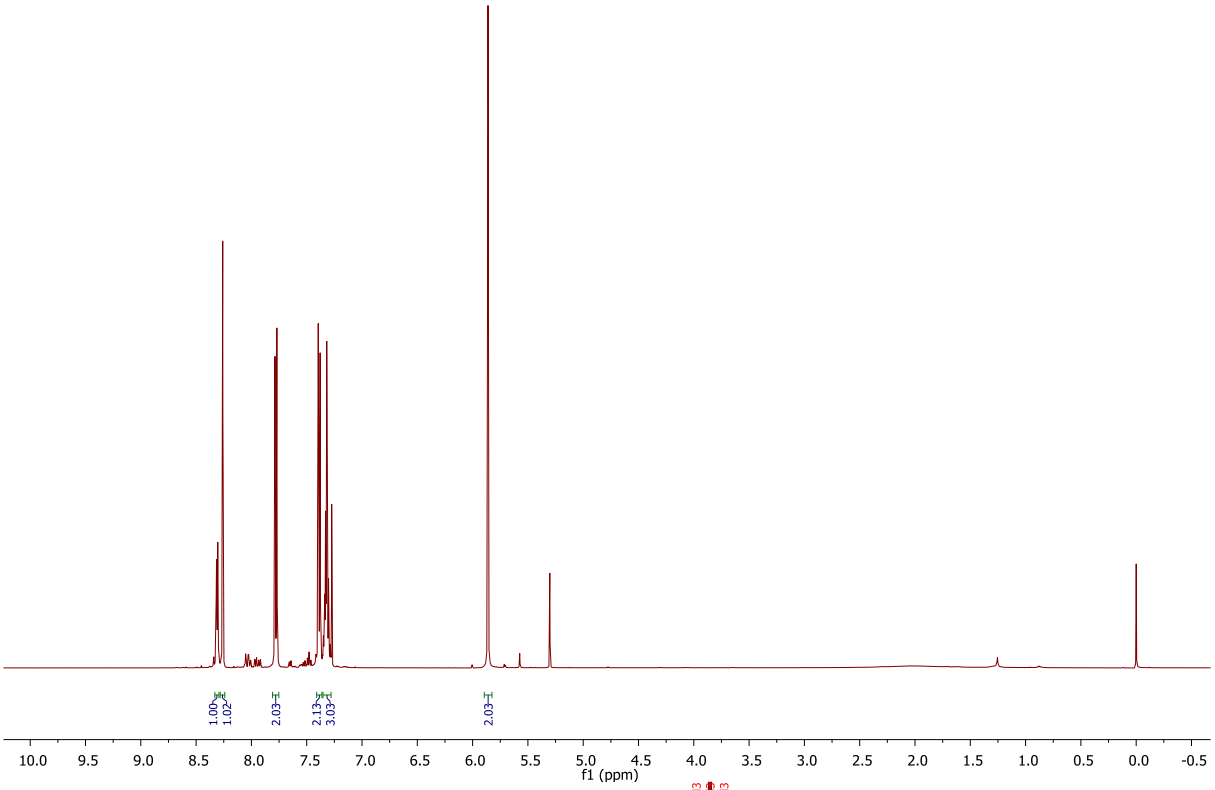
3Ae

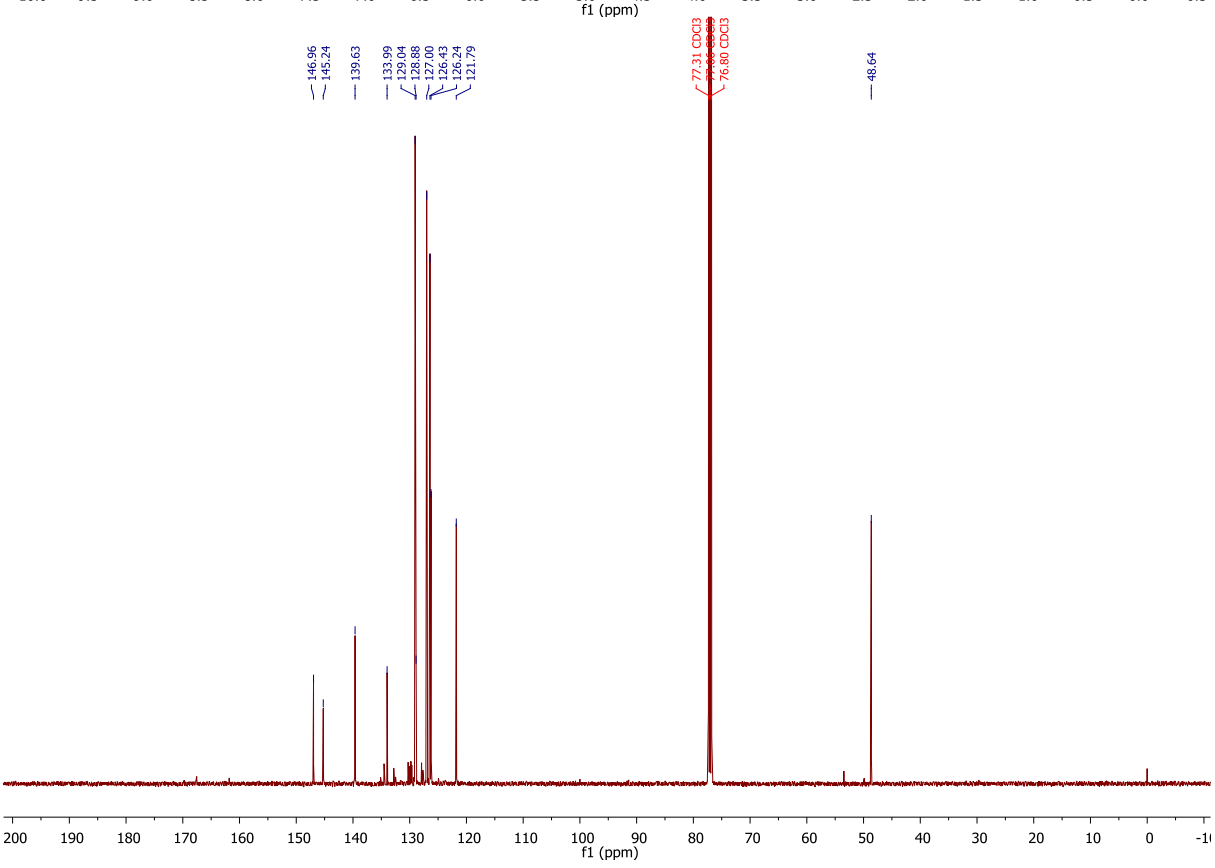

1.00
0.99
1.99
2.01
3.02
2.02
f1 (ppm)

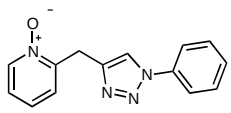

146.56
145.00
139.64
133.84
133.83
130.41
130.15
129.89
129.64
126.62
126.36
126.21
125.88
125.84
125.81
125.16
123.00
122.56
77.29 CDCl3
76.79 CDCl3
48.71
f1 (ppm)



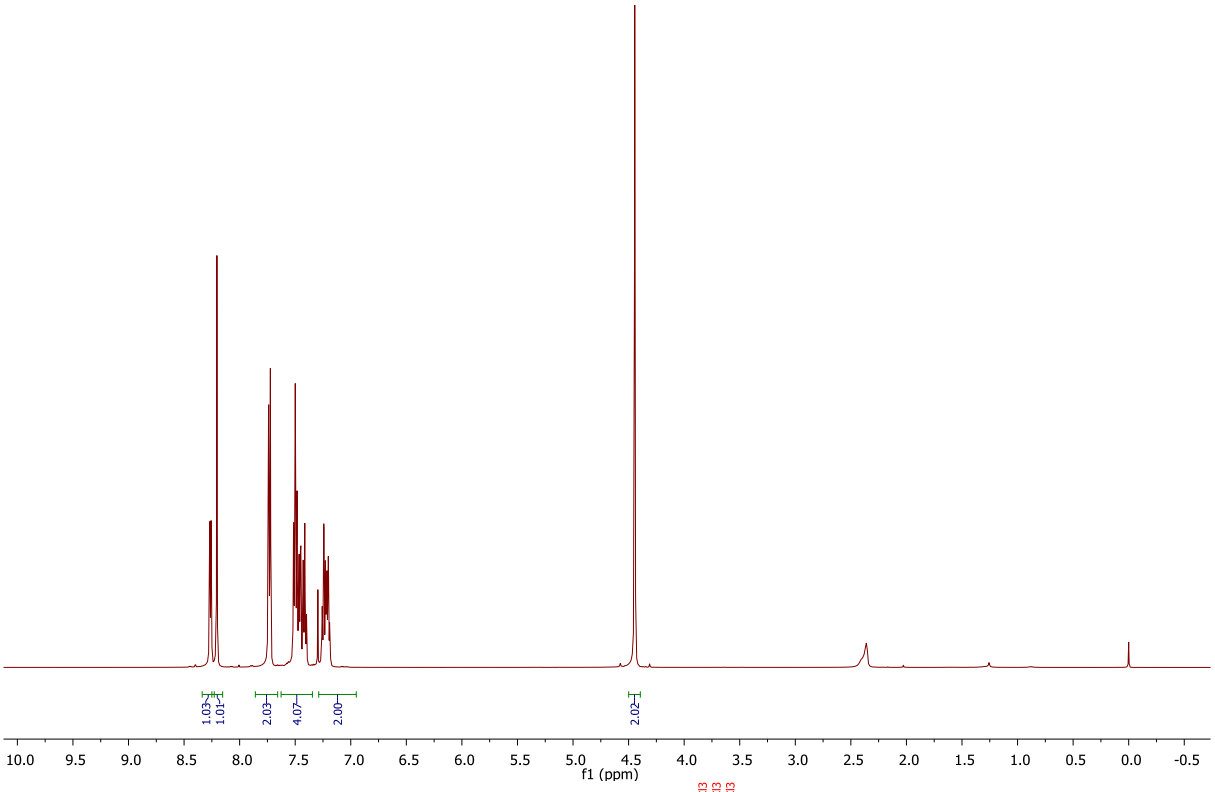
3Af

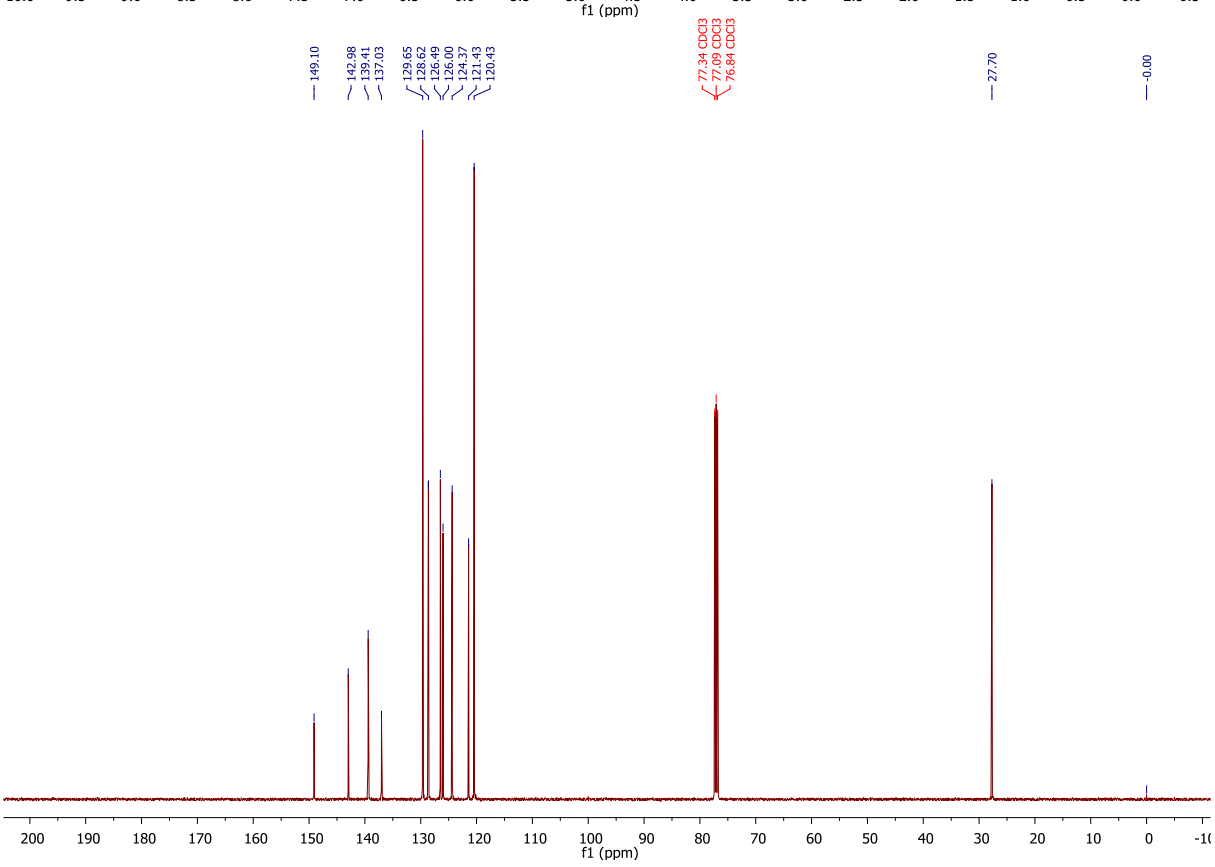

1.00
1.02
2.03
2.13
3.03
2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

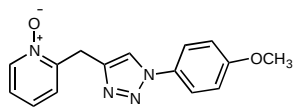

146.96
145.24
139.63
133.99
129.04
128.88
127.00
126.43
126.24
121.79
77.31 CDCl3
76.80 CDCl3
48.64
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



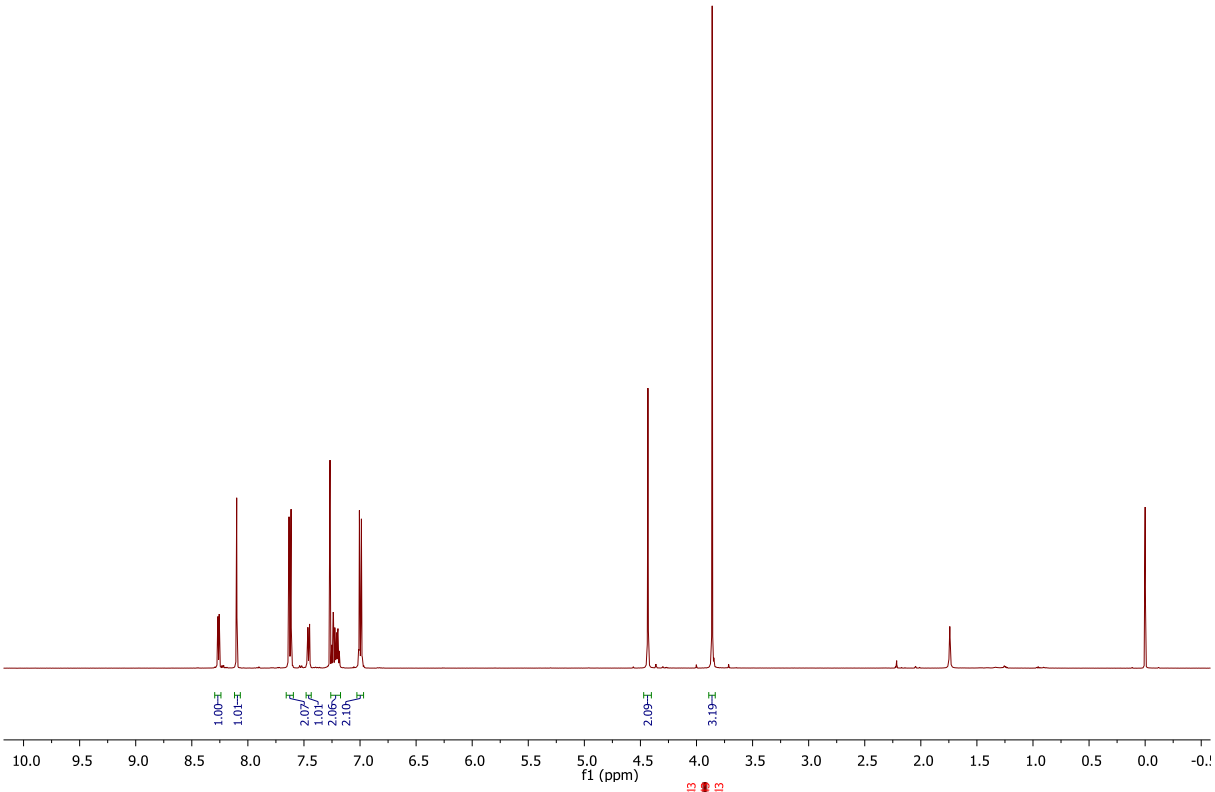
3Ba

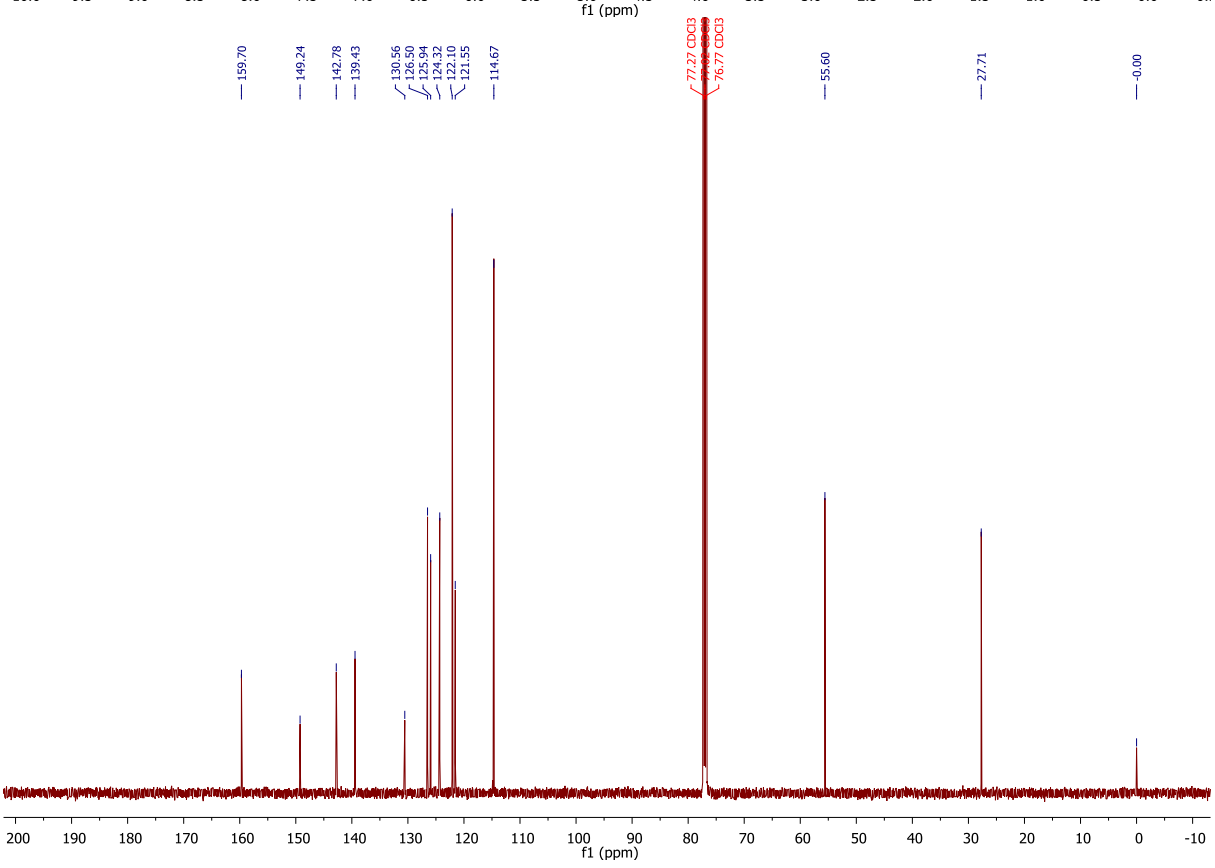

1.03
1.01
2.03
4.07
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

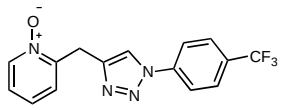

149.10
142.98
139.41
137.03
129.65
128.62
126.49
126.00
124.37
121.43
120.43
77.34 CDCl3
77.09 CDCl3
76.84 CDCl3
27.70
-0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



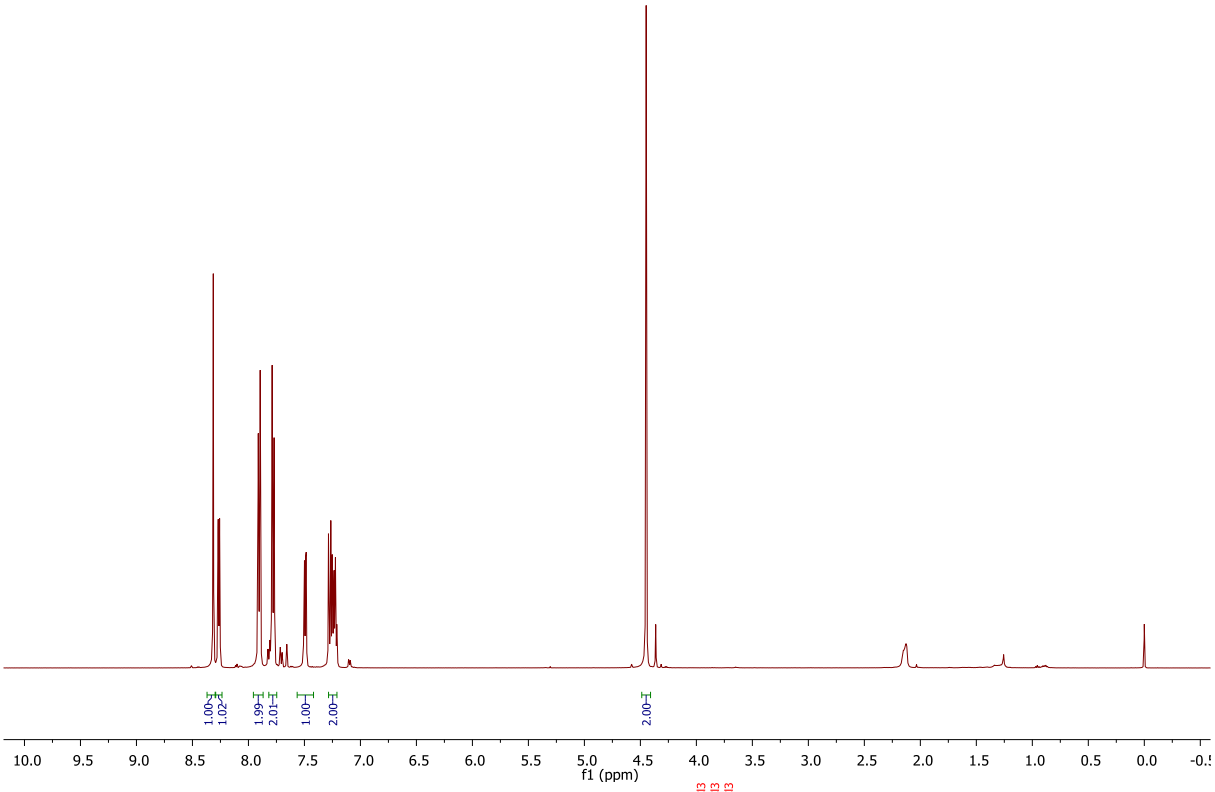
3Bc

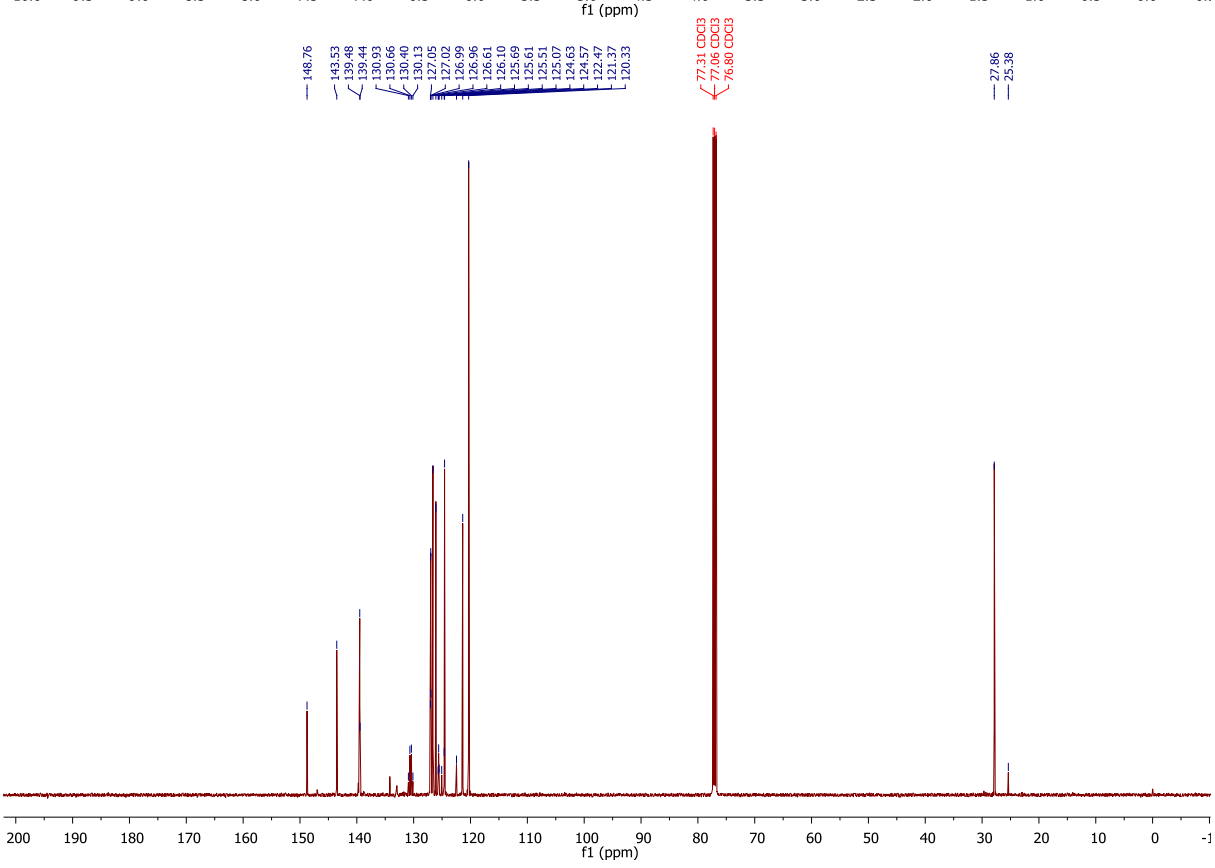

1.00
1.01
2.07
1.01
2.06
2.10
2.09
3.19
f1 (ppm)

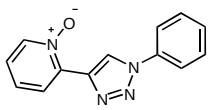

159.70
149.24
142.78
139.43
130.56
126.50
125.94
124.32
122.10
121.55
114.67
77.27 CDCl3
76.77 CDCl3
55.60
27.71
-0.00
f1 (ppm)



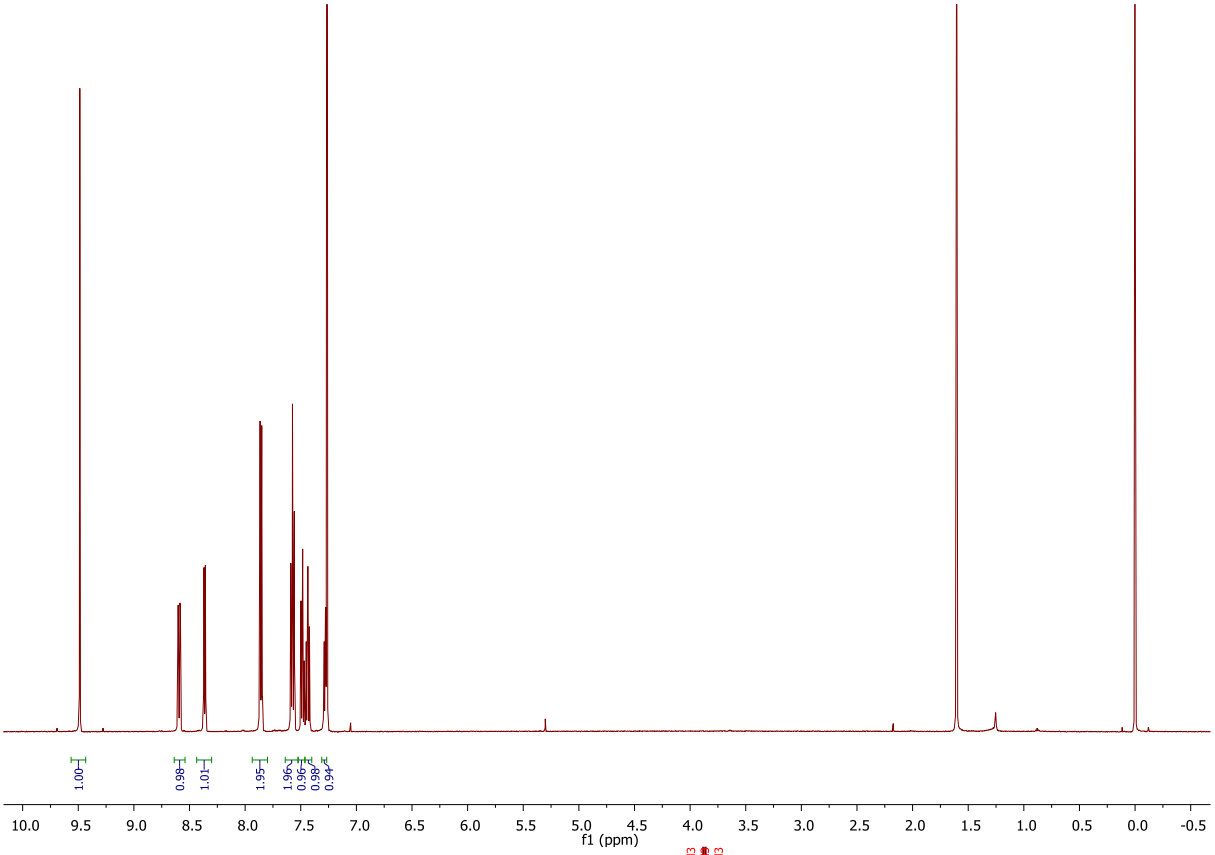
3Be

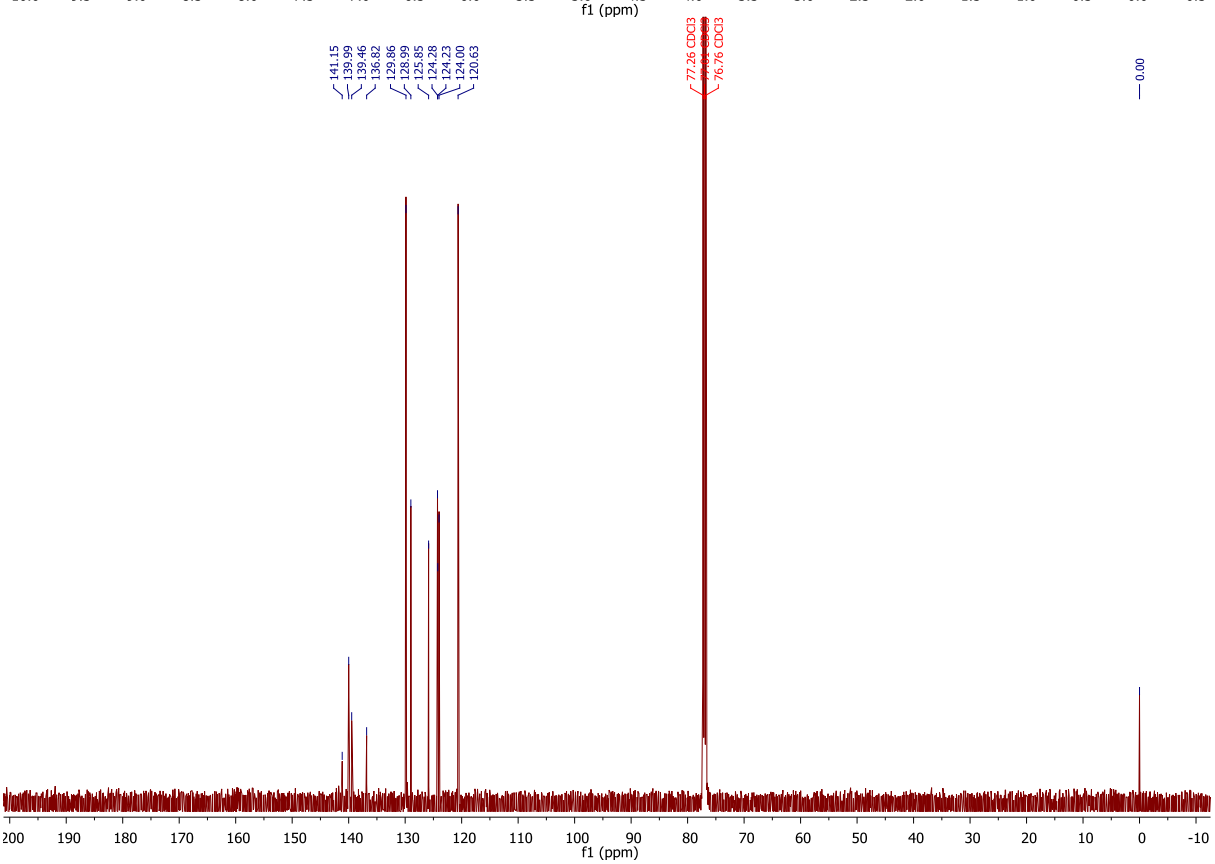

1.00
1.02
1.99
2.01
1.00
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

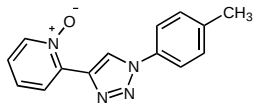

148.76
143.53
139.48
139.44
130.93
130.66
130.40
130.13
127.05
127.02
126.99
126.96
126.61
126.10
125.69
125.61
125.51
125.07
124.63
124.57
122.47
121.37
120.33
77.31 CDCl3
77.06 CDCl3
76.80 CDCl3
27.86
25.38
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



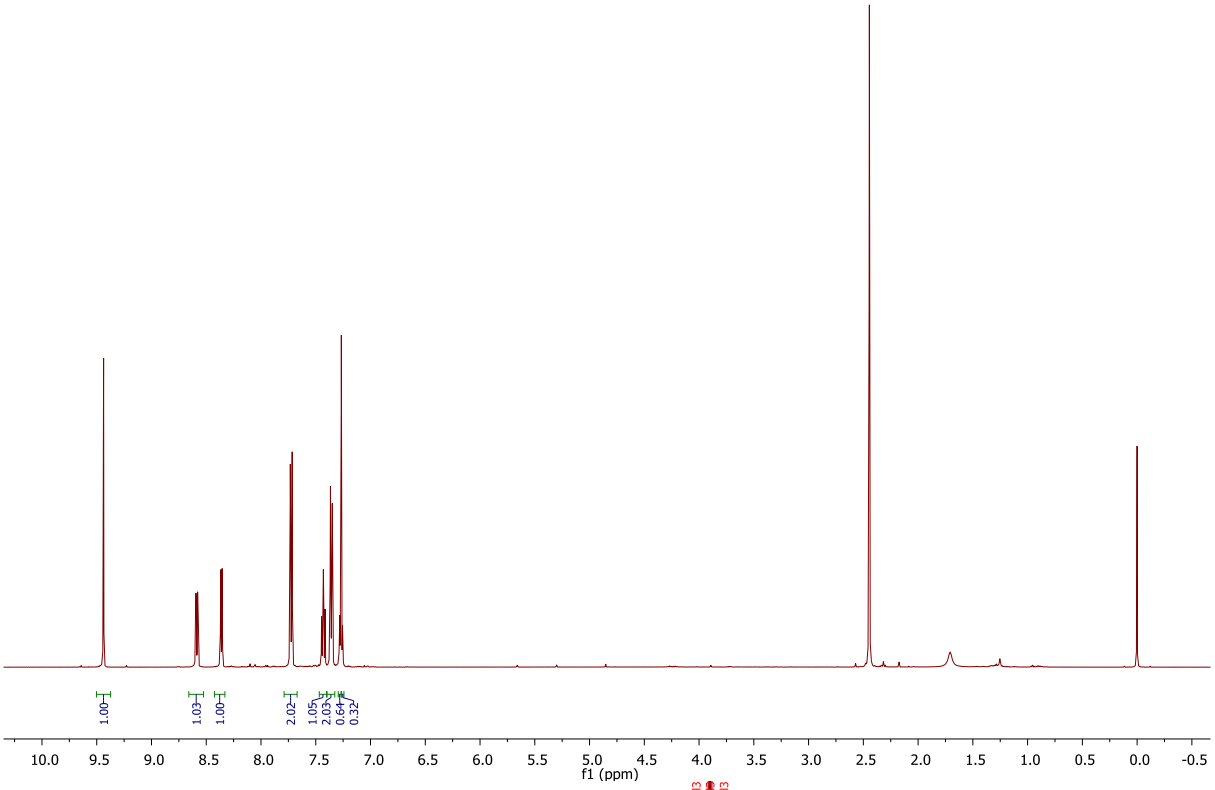
3Da

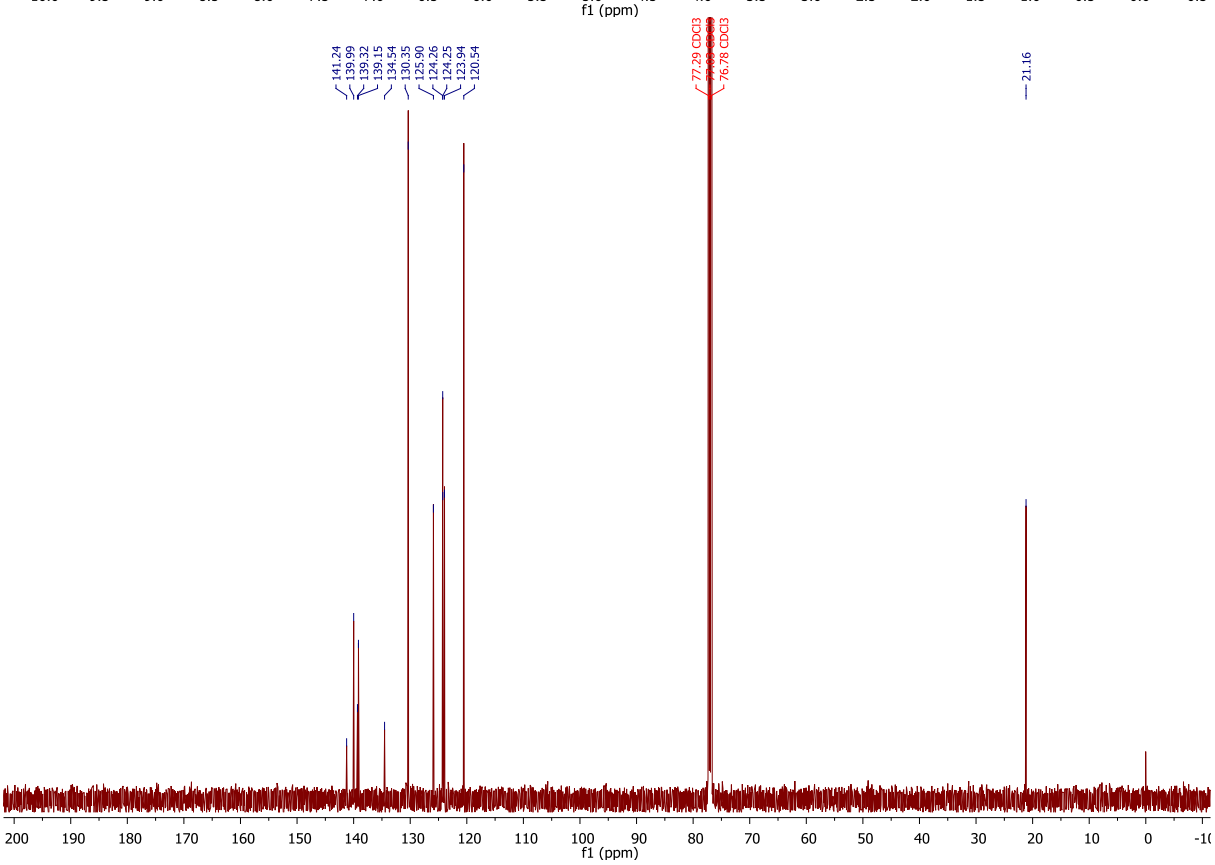

1.00
0.98
1.01
1.95
1.96
0.96
0.98
0.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

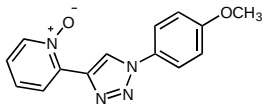

141.15
139.99
139.46
136.82
129.86
128.99
125.85
124.28
124.23
124.00
120.63
77.26 CDCl3
76.76 CDCl3
0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CH3
O
N
N
N

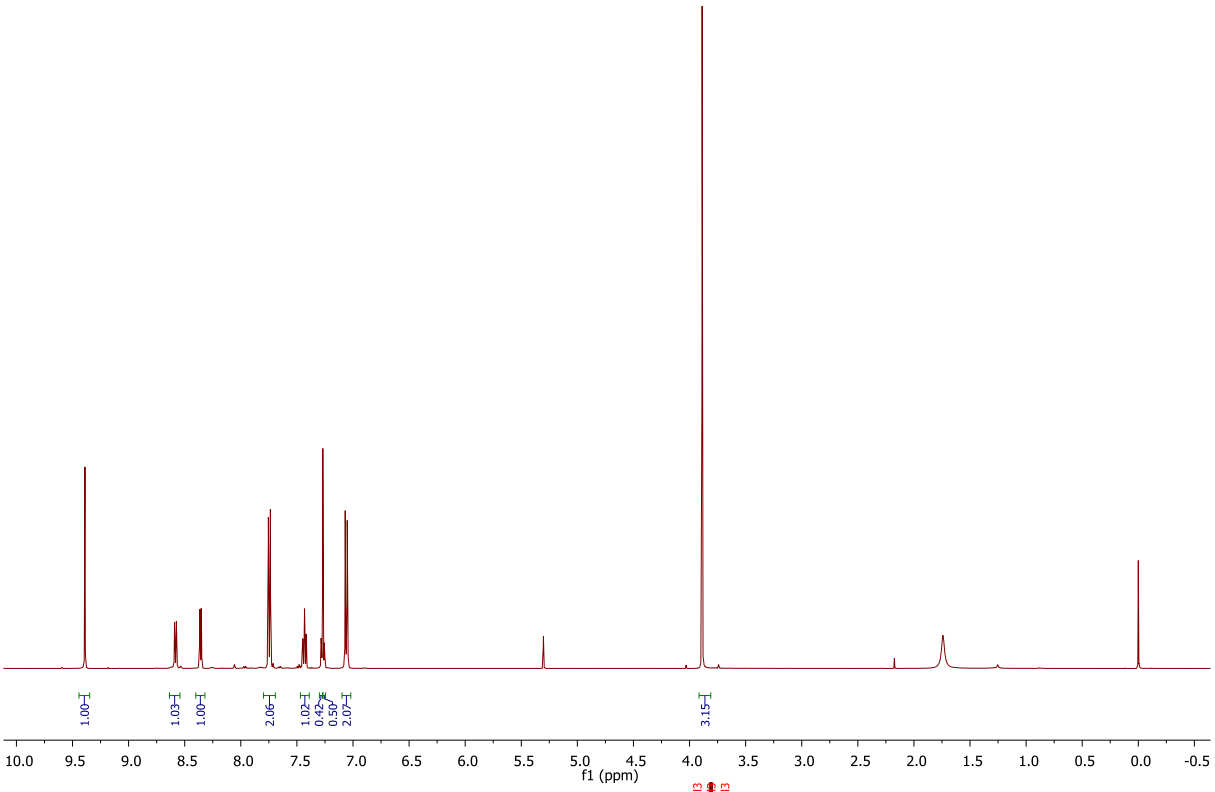
3Db

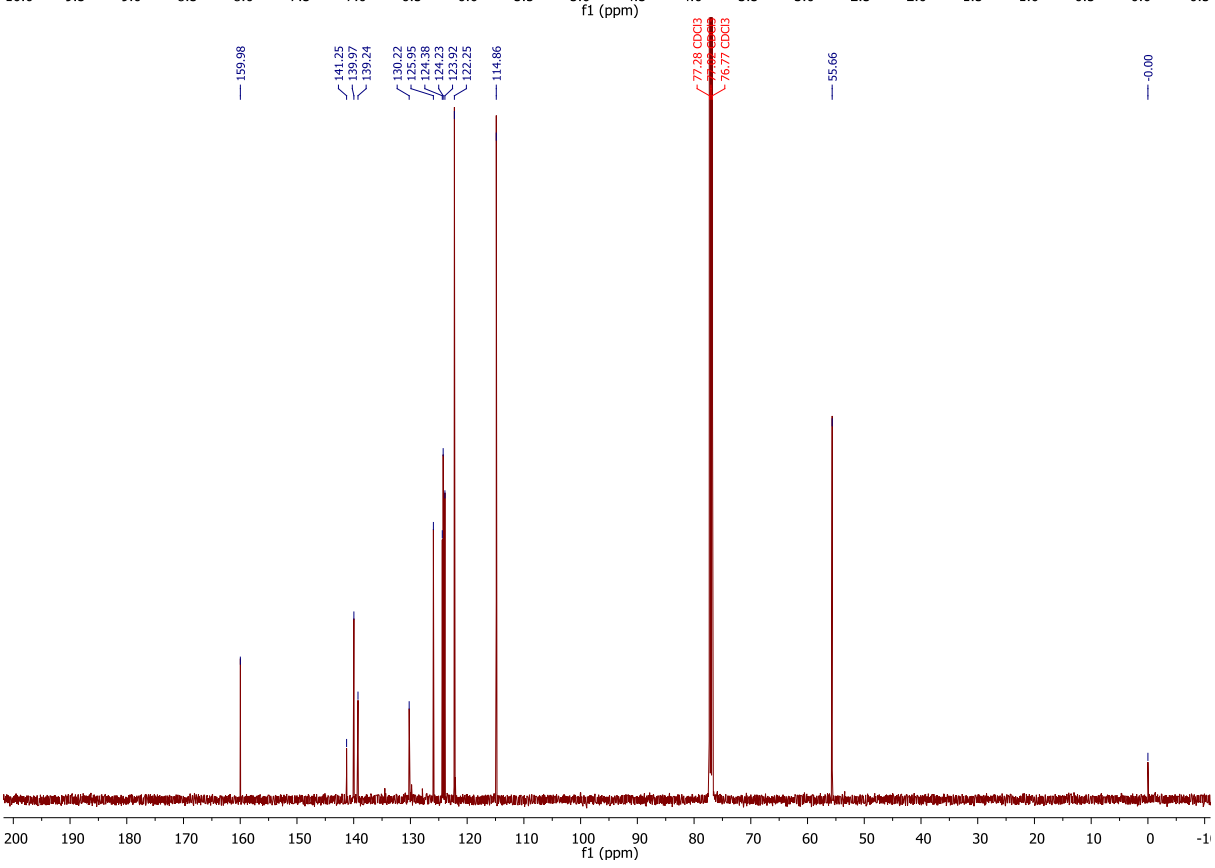

1.00
1.03
1.00
2.02
1.05
2.03
0.64
0.32
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

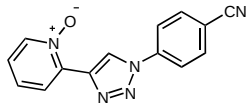

141.24
139.99
139.32
139.15
134.54
130.35
125.90
124.26
124.25
123.94
120.54
77.29 CDCl3
76.78 CDCl3
21.16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OCH3
N
O
N
N
N

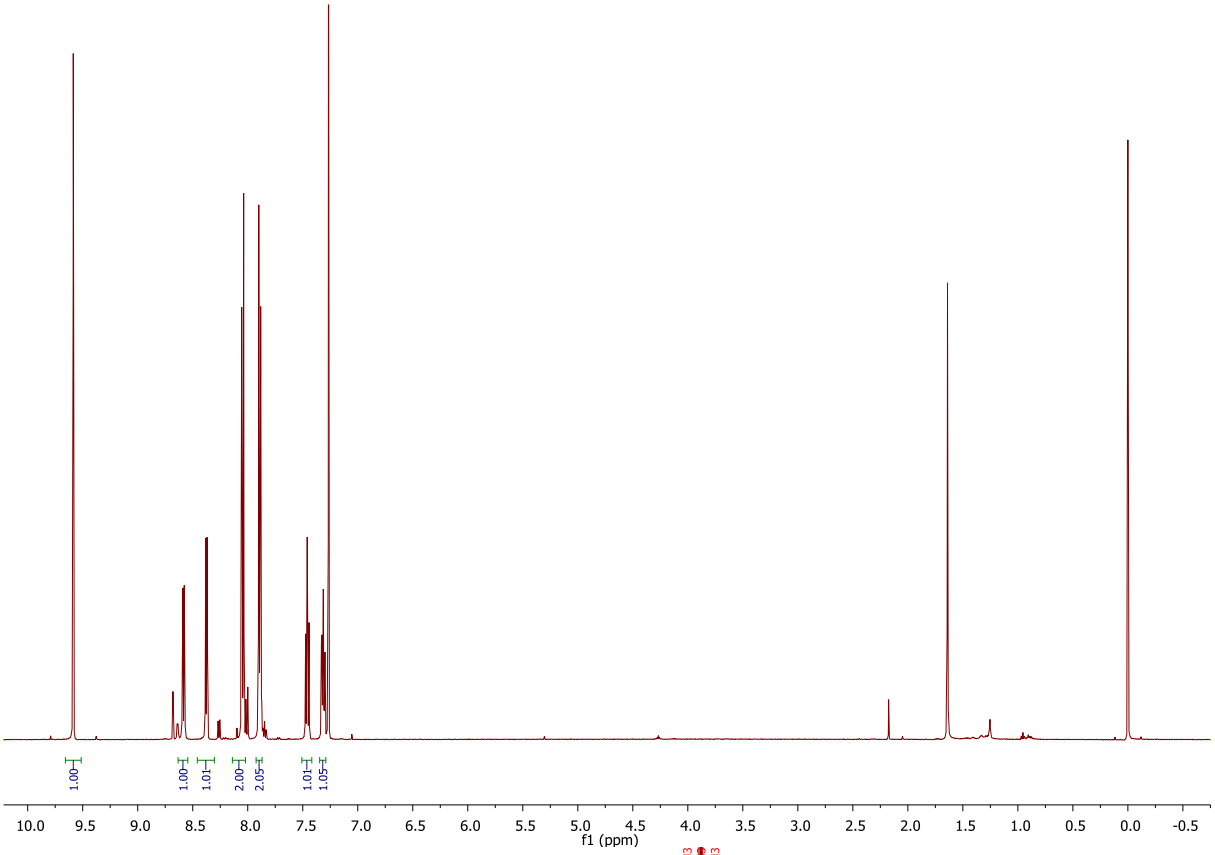
3Dc

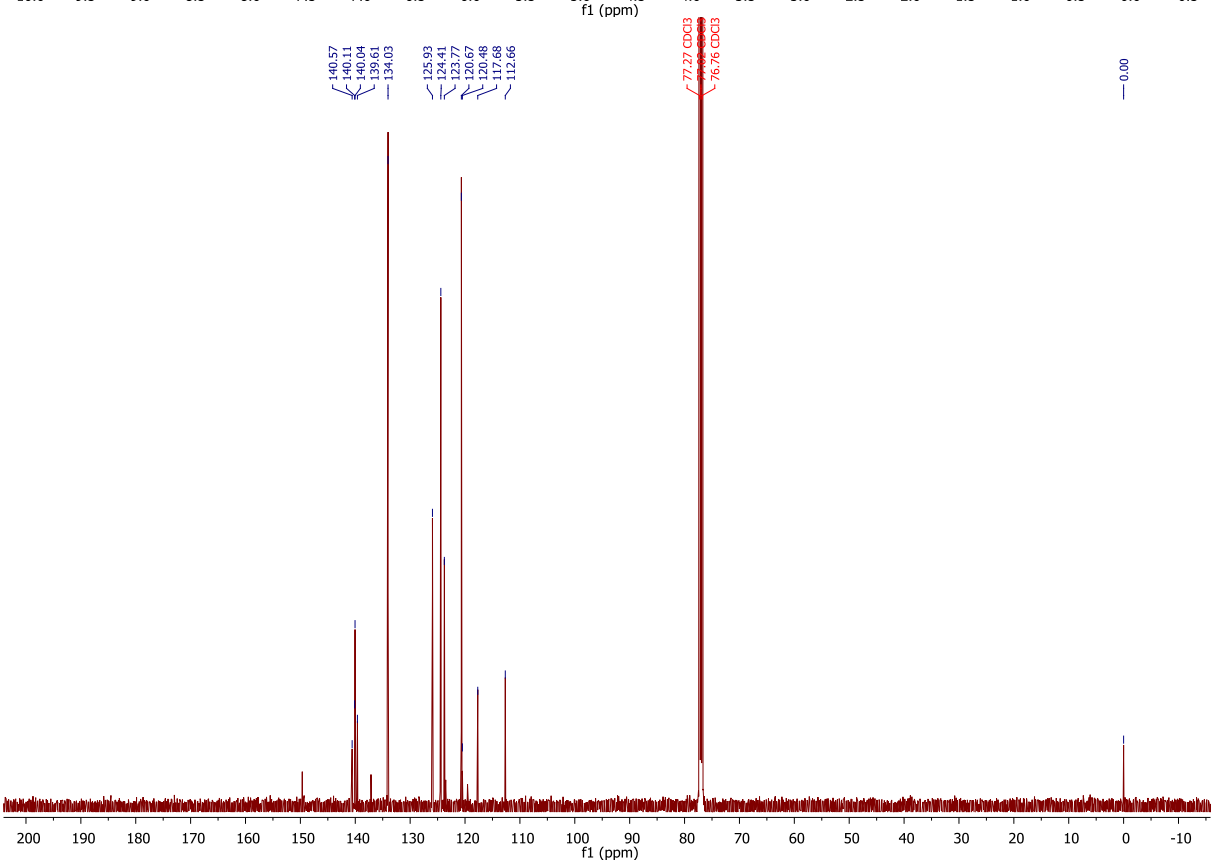

1.00
1.03
1.00
2.06
1.02
0.42
0.50
2.07
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

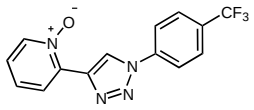

159.98
141.25
139.97
139.24
130.22
125.95
124.38
124.23
123.92
122.25
114.86
77.28 CDCl3
76.77 CDCl3
55.66
-0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CN
N
N
N
O

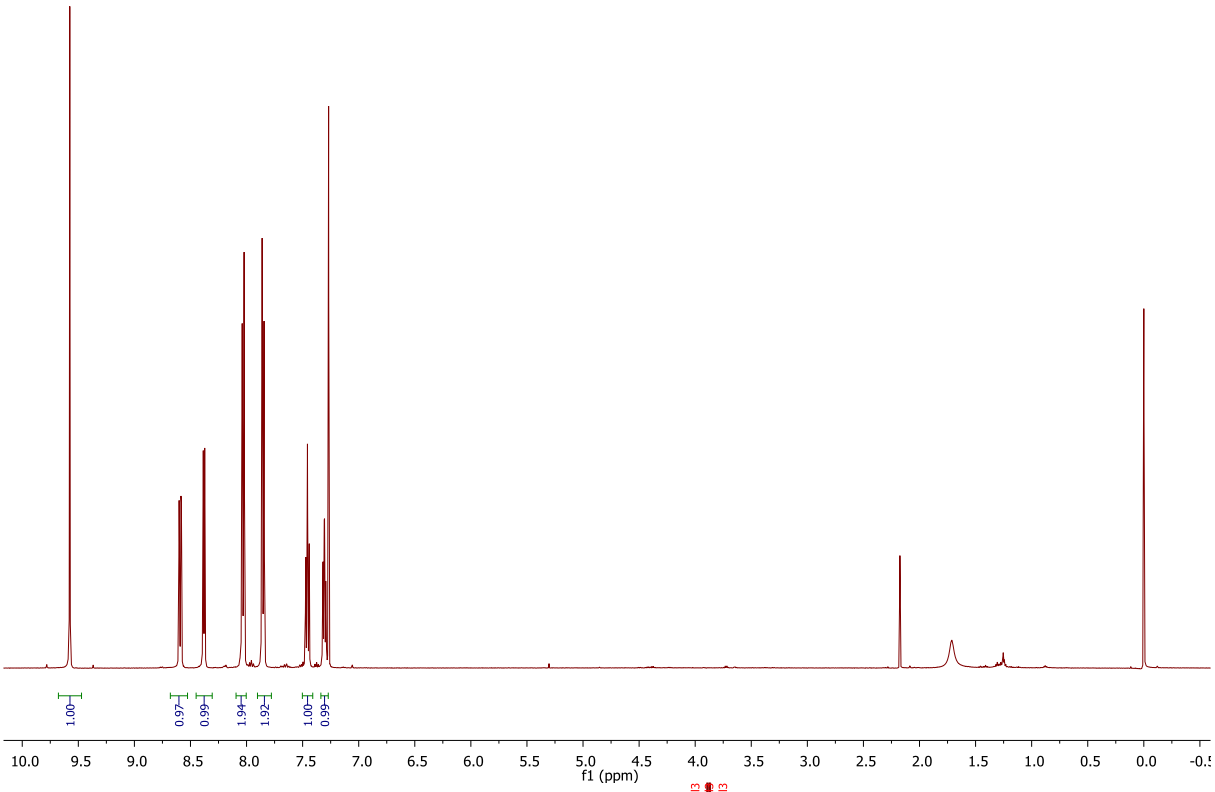
3Dd

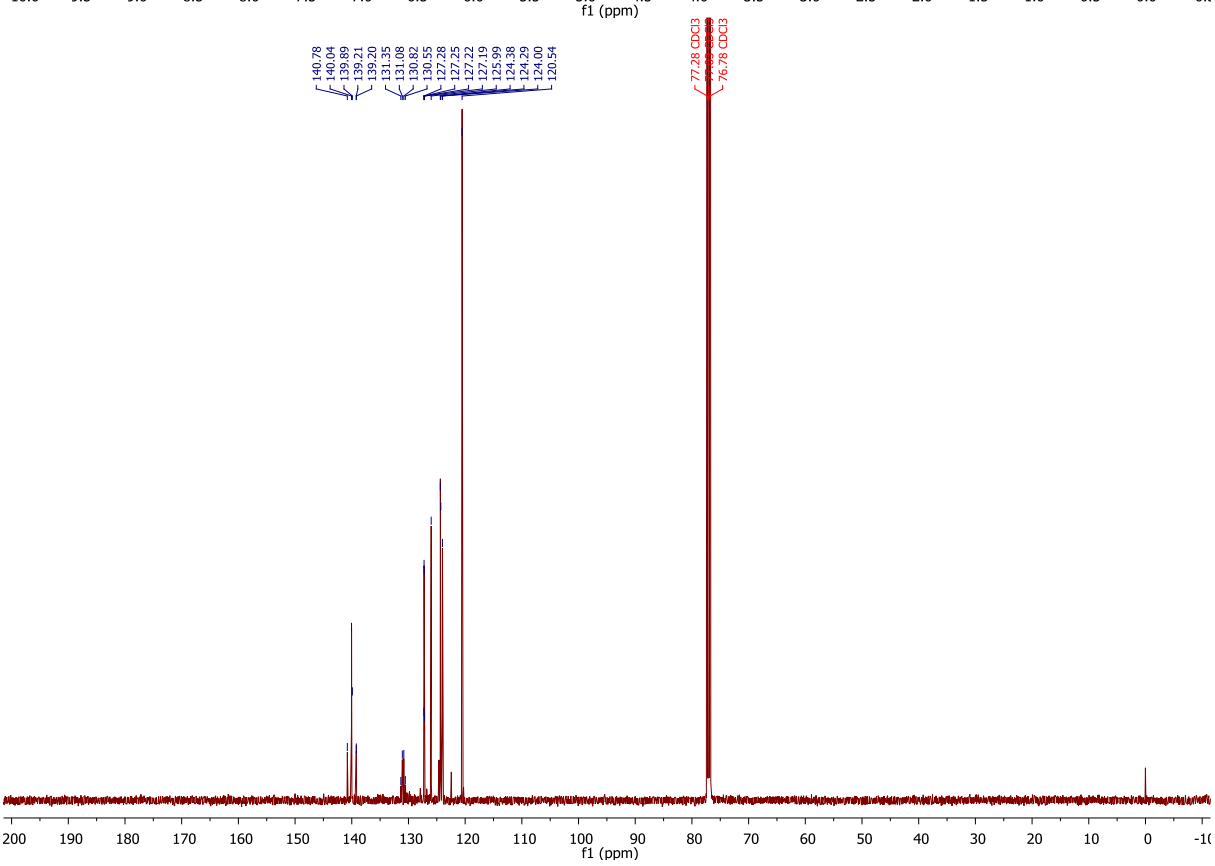

1.00
1.00
1.01
2.00
2.05
1.01
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

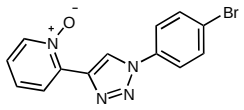

140.57
140.11
140.04
139.61
134.03
125.93
124.41
123.77
120.67
120.48
117.68
112.66
77.27 CDCl3
76.76 CDCl3
0.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



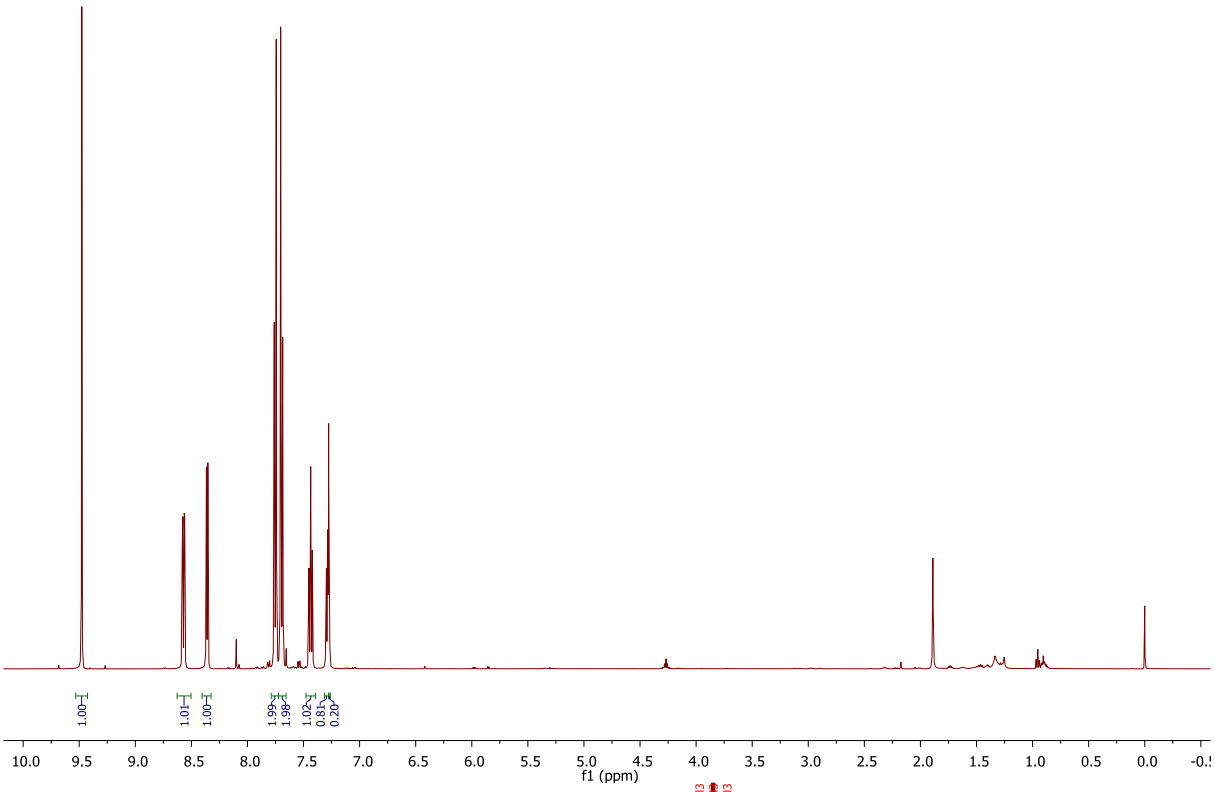
3De

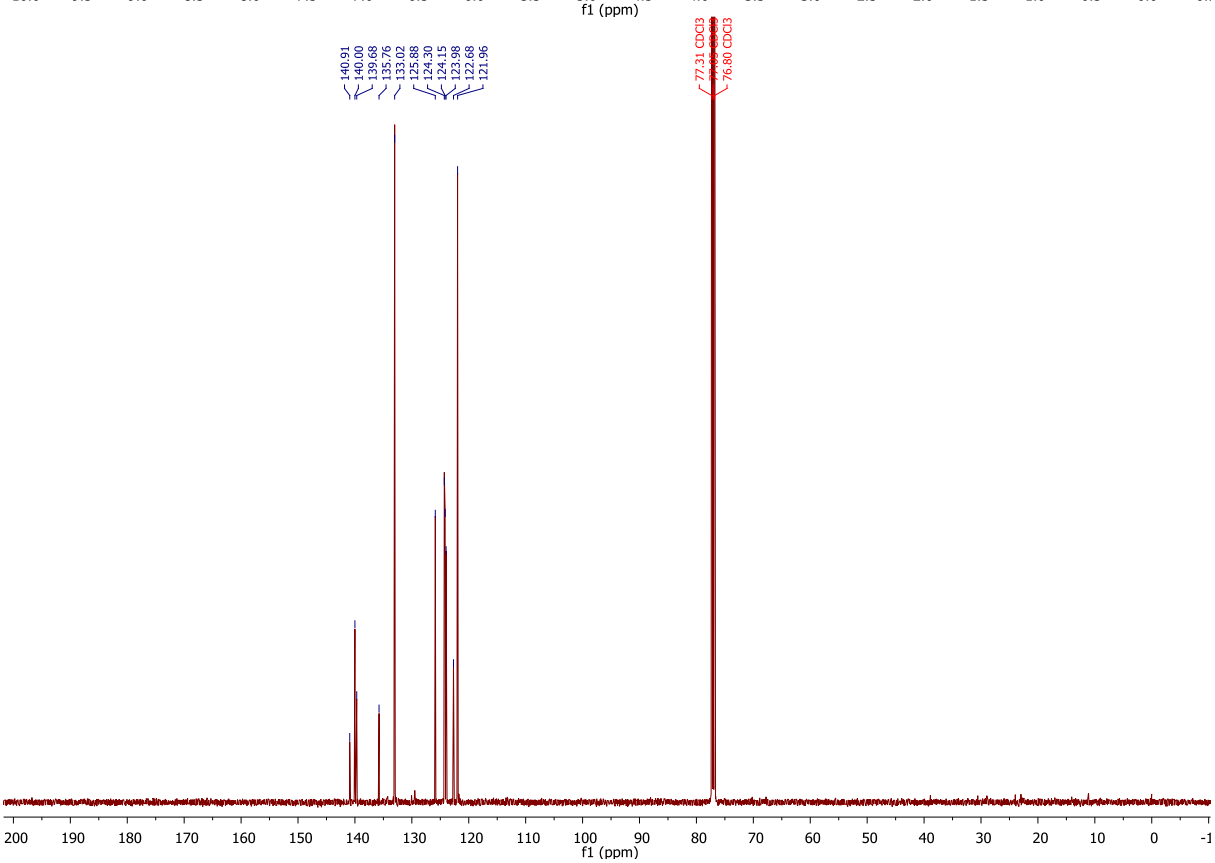

1.00
0.97
0.99
1.94
1.92
1.00
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

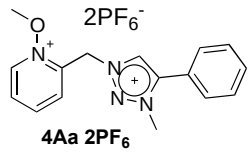

140.78
140.04
139.89
139.21
139.20
131.35
131.08
130.82
130.55
127.28
127.25
127.22
127.19
125.99
124.38
124.29
124.00
120.54
77.28 CDCl3
76.78 CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
O
N
N
N

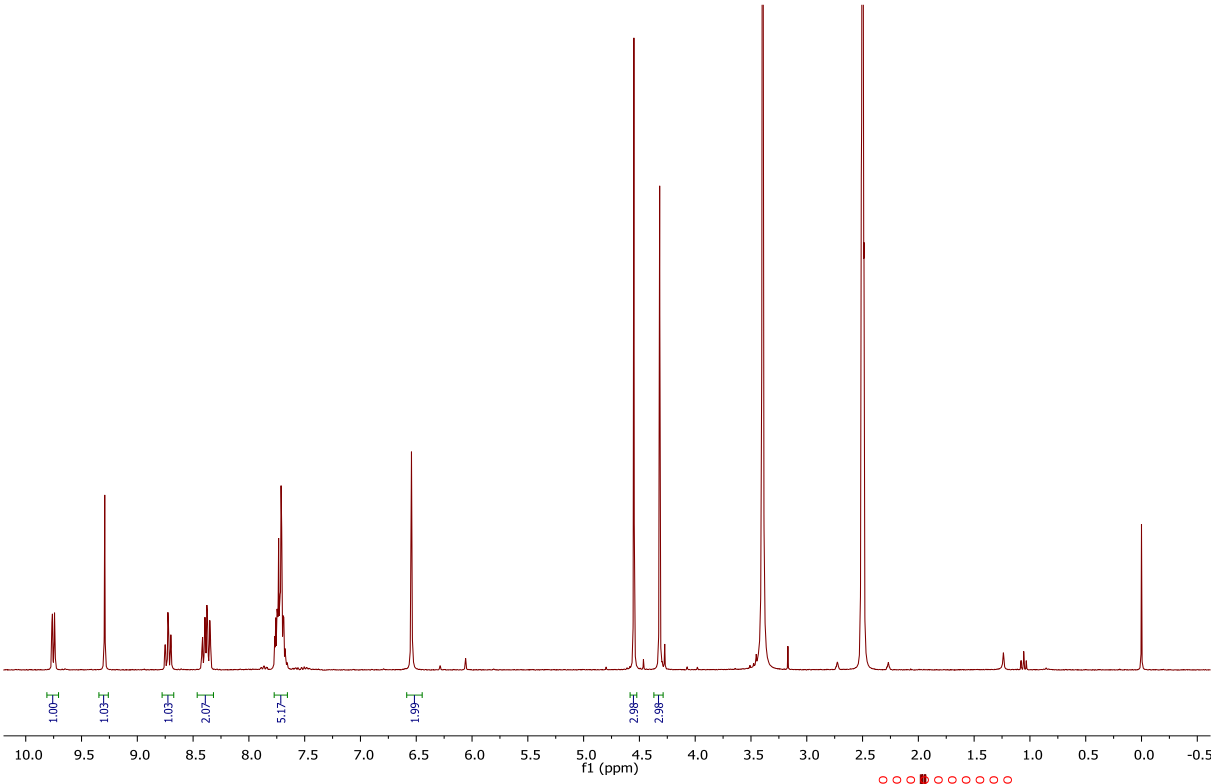
3Dg

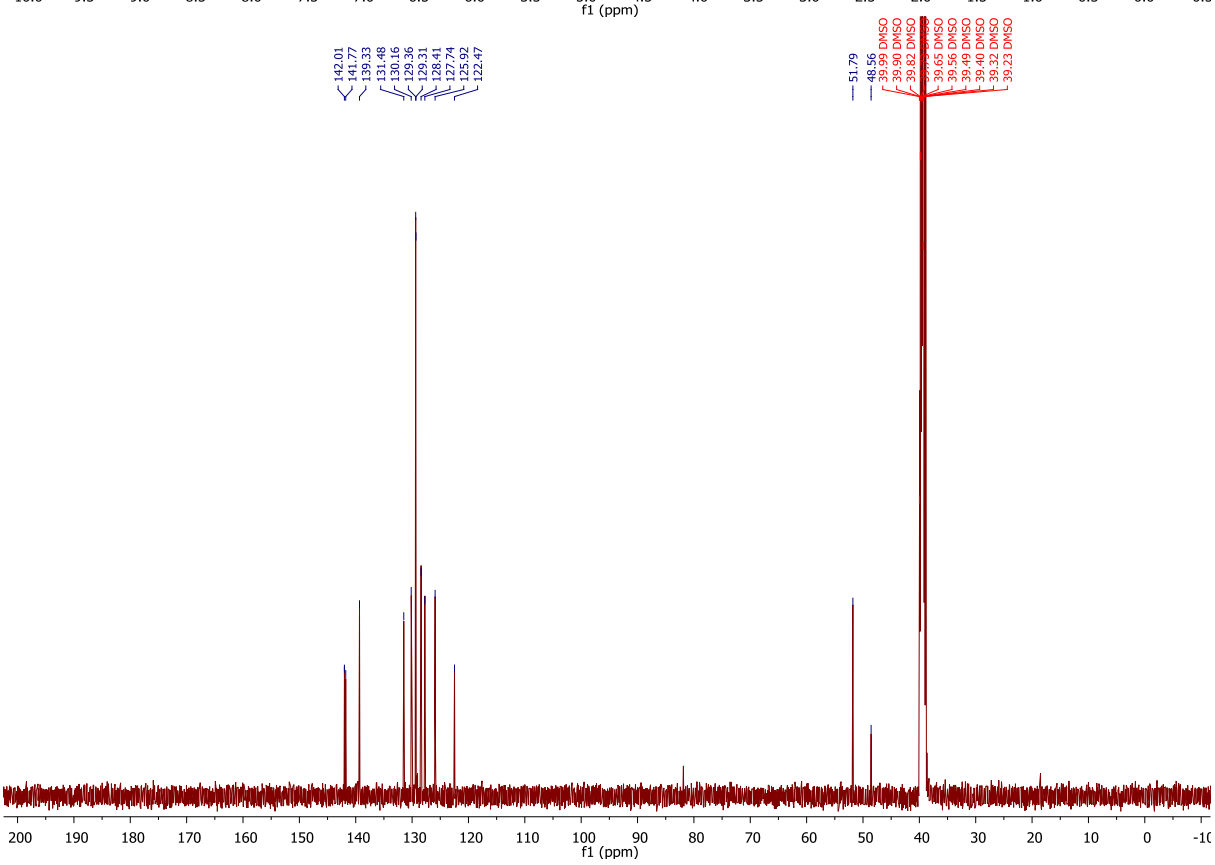

1.00
1.01
1.00
1.99
1.98
1.02
0.81
0.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

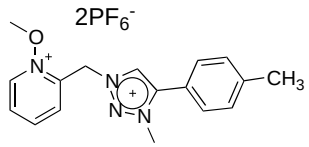

140.91
140.00
139.68
135.76
133.02
125.88
124.30
124.15
123.98
122.68
121.96
77.31 CDCl3
76.80 CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2PF6-

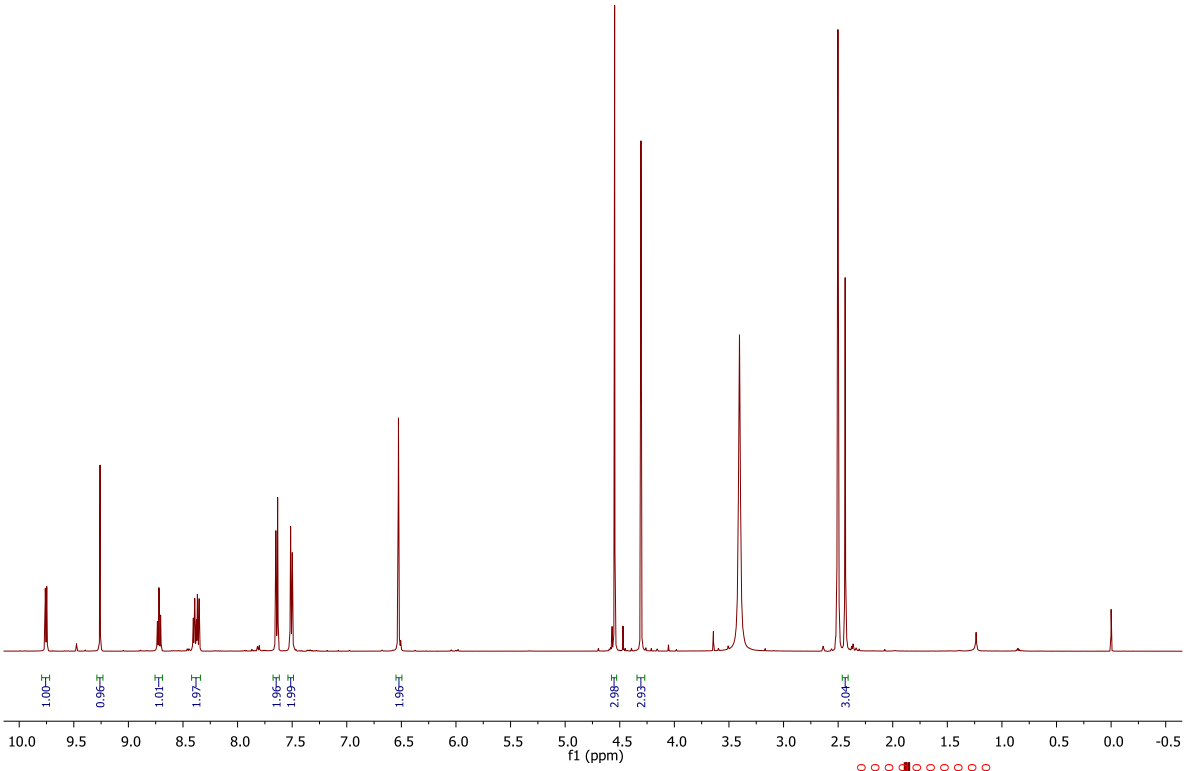
4Aa 2PF$_6$

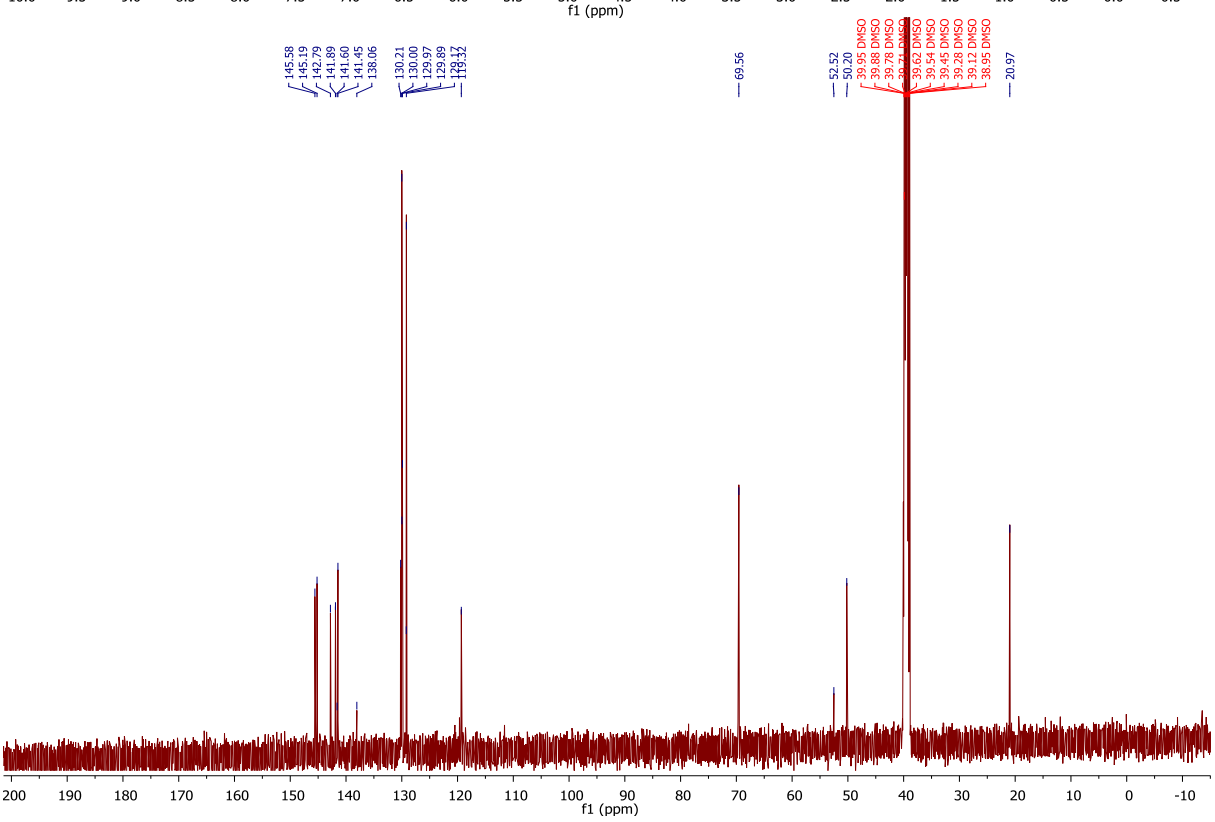

1.00
1.03
1.03
2.07
5.17
1.99
2.98
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

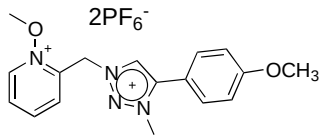

142.01
141.77
139.33
131.48
130.16
129.36
129.31
128.41
127.74
125.92
122.47
51.79
48.56
39.99 DMSO
39.90 DMSO
39.82 DMSO
39.65 DMSO
39.56 DMSO
39.49 DMSO
39.40 DMSO
39.32 DMSO
39.23 DMSO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2PF6-
O
N+
N
N
N
CH3

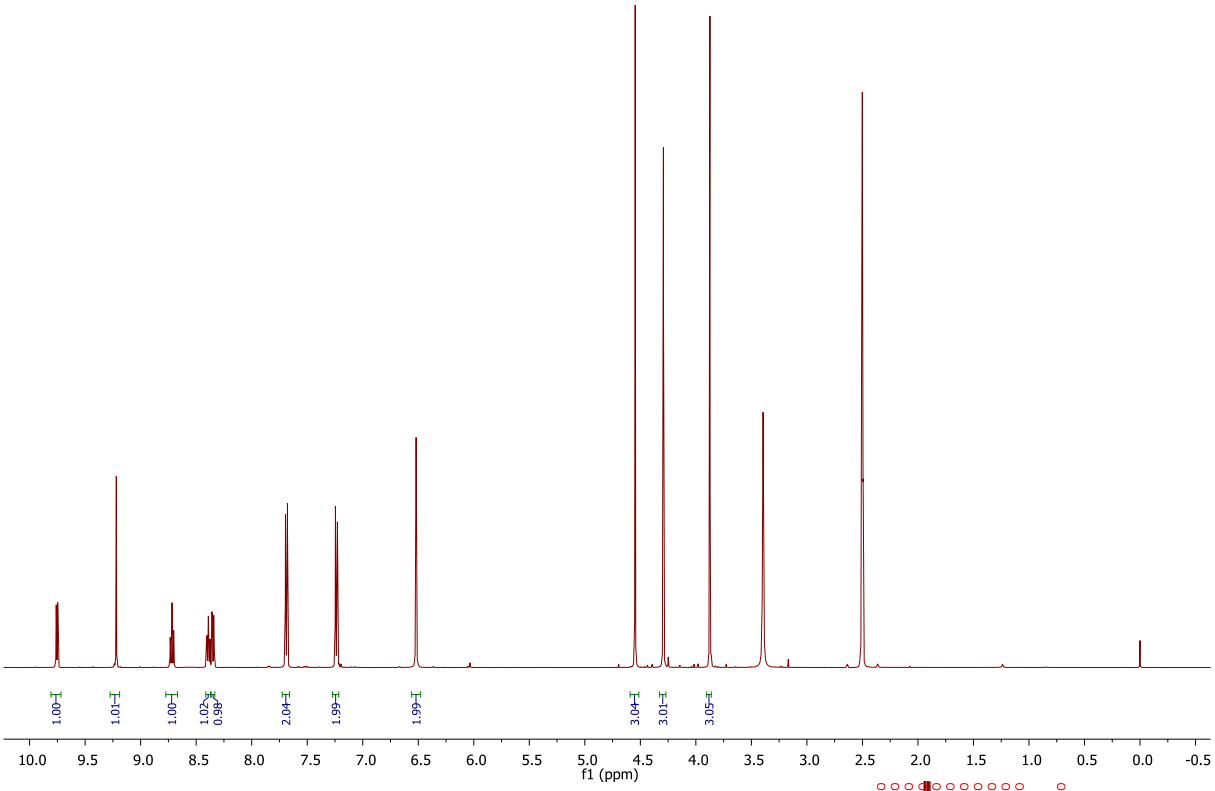
4Ab 2PF$_6$

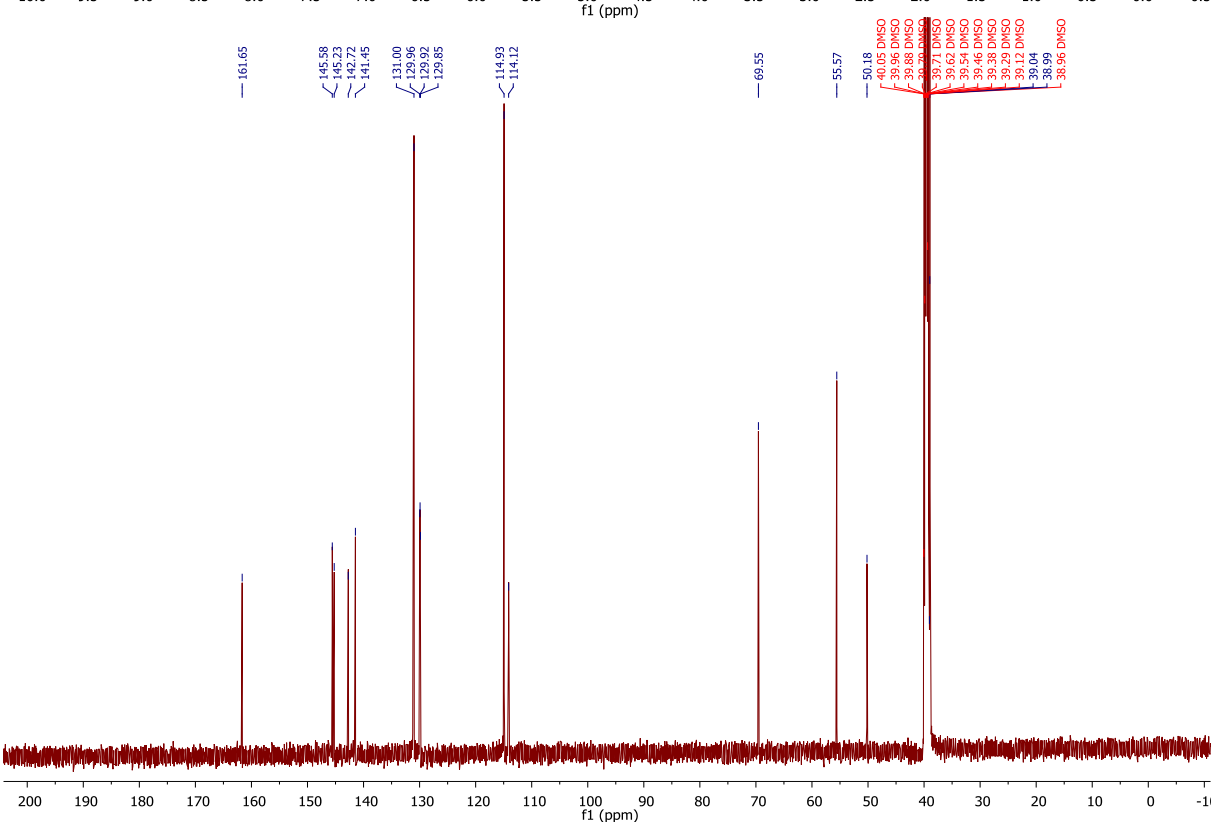

1.00
0.96
1.01
1.97
1.96
1.99
1.96
2.98
2.93
3.04
f1 (ppm)

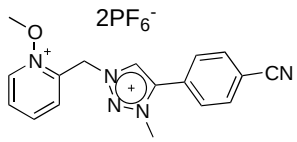

145.58
145.19
142.79
141.89
141.60
141.45
138.06
130.21
130.00
129.97
129.89
121.32
69.56
52.52
50.20
39.95 DMSO
39.88 DMSO
39.79 DMSO
39.71 DMSO
39.62 DMSO
39.54 DMSO
39.45 DMSO
39.28 DMSO
39.12 DMSO
38.95 DMSO
20.97
f1 (ppm)


2PF6-
O
N+
N
N
N
OCH3

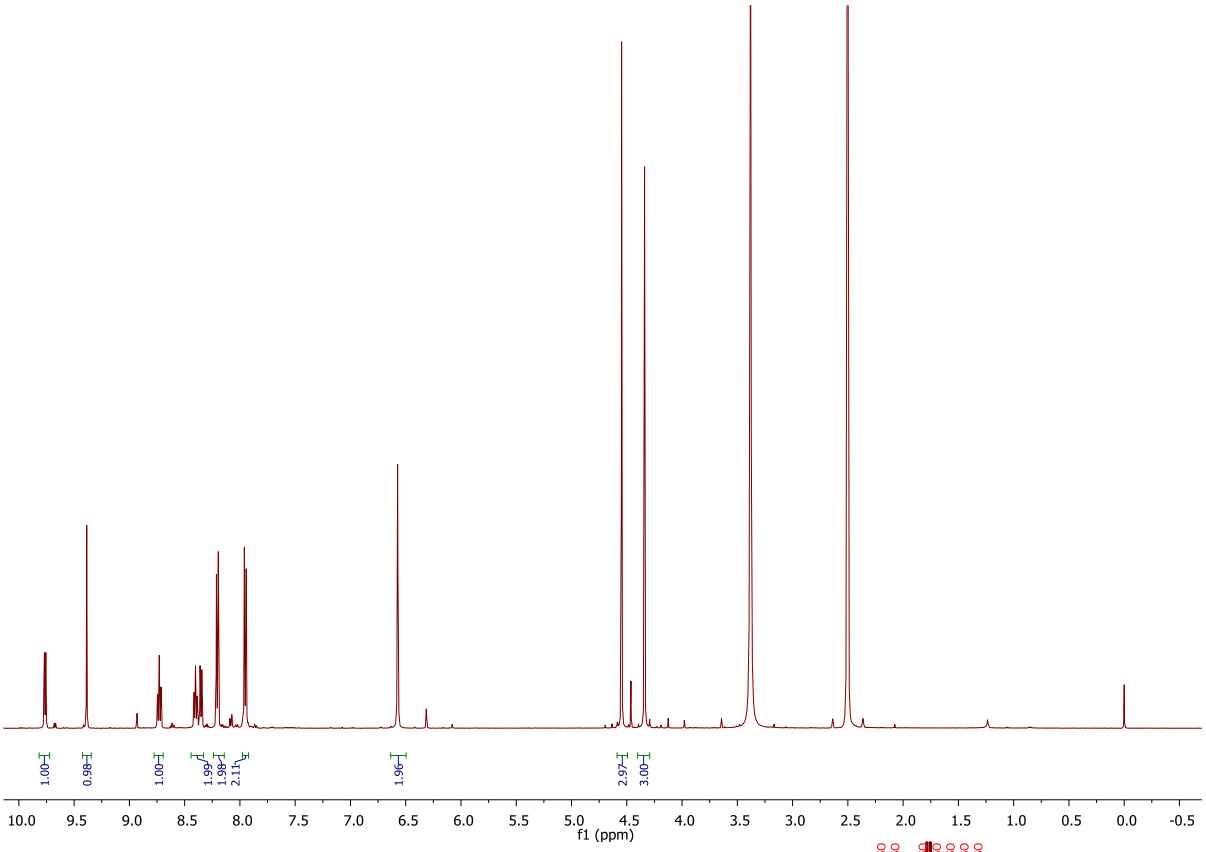
4Ac 2PF$_6$

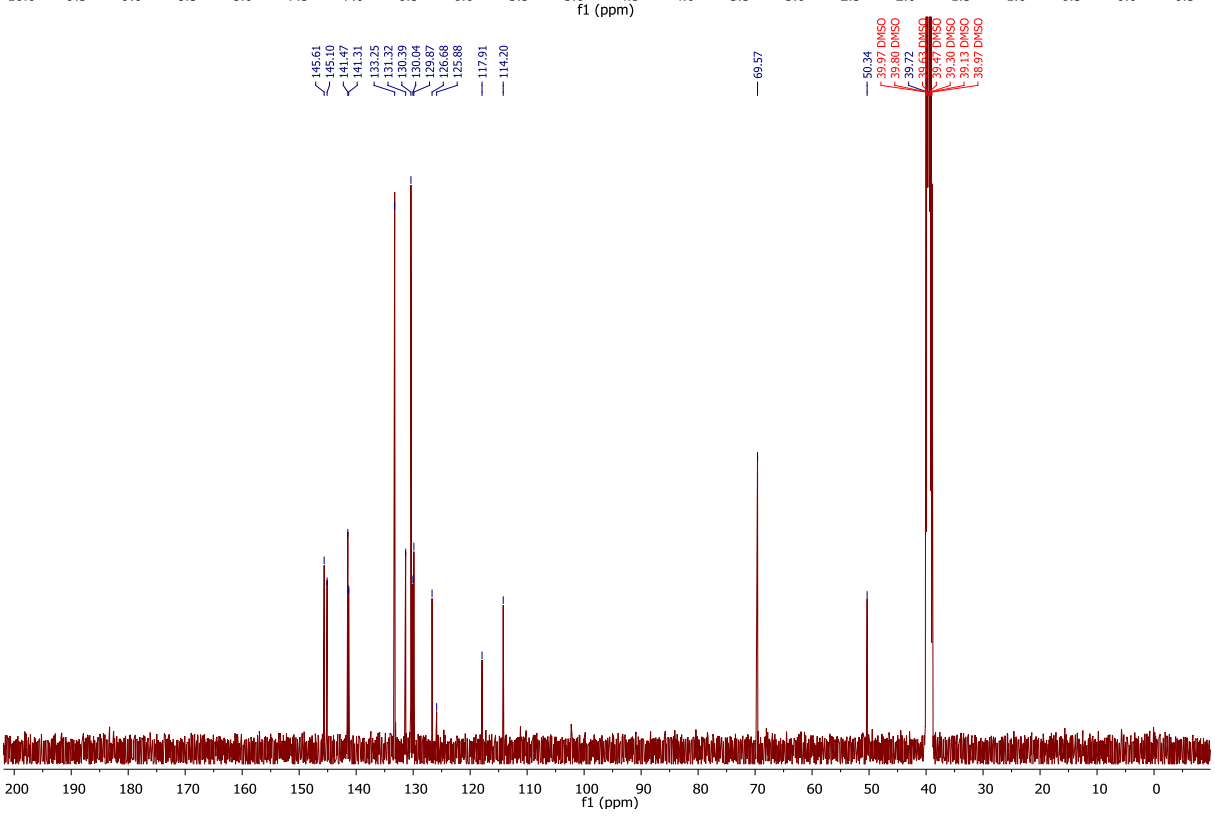

1.00
1.01
1.00
1.02
0.98
2.04
1.99
1.99
3.04
3.01
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

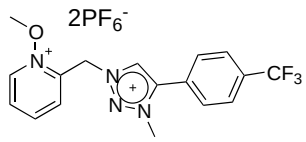

161.65
145.58
145.23
142.72
141.45
131.00
129.96
129.92
129.85
114.93
114.12
69.55
55.57
50.18
40.05 DMSO
39.96 DMSO
39.88 DMSO
39.79 DMSO
39.71 DMSO
39.62 DMSO
39.54 DMSO
39.46 DMSO
39.38 DMSO
39.29 DMSO
39.12 DMSO
39.04
38.99
38.96 DMSO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2PF6-
O
N+
N
N
N
CN

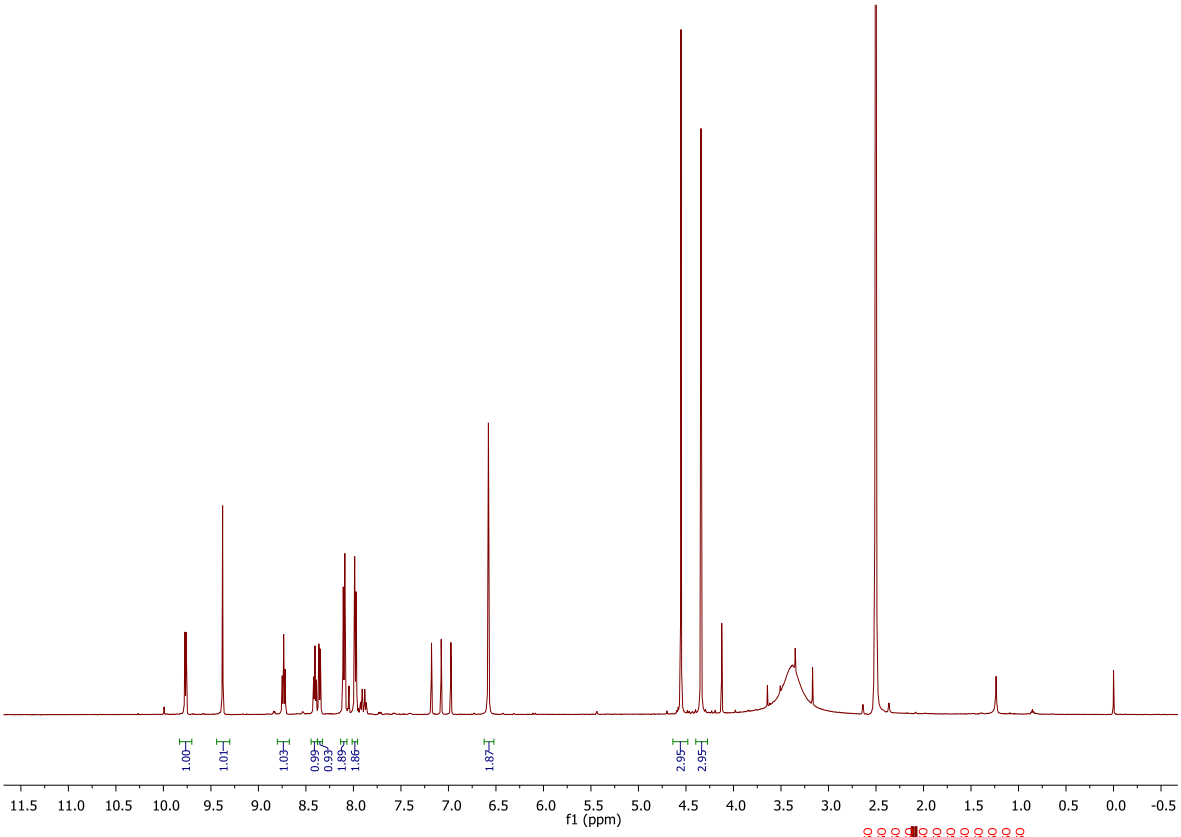
4Ad 2PF$_6$

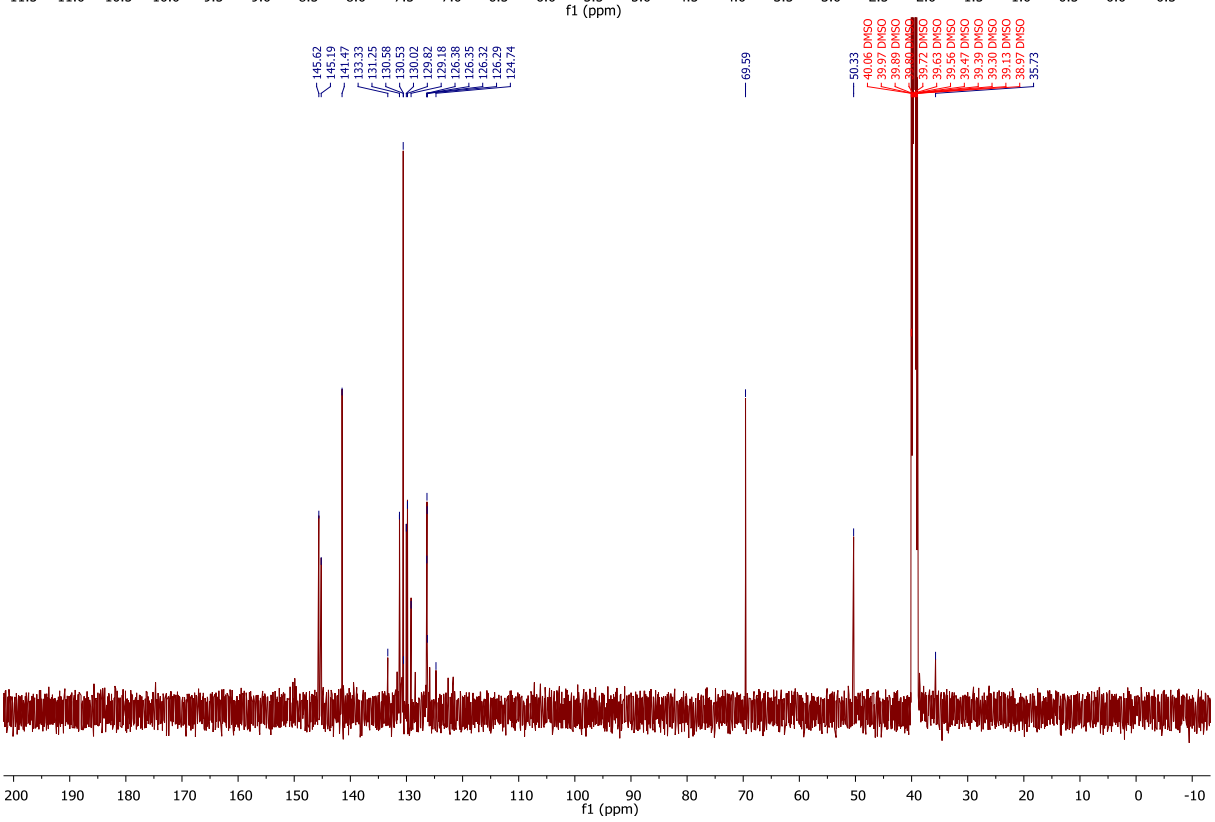

1.00
0.98
1.00
1.99
1.98
2.11
1.96
2.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

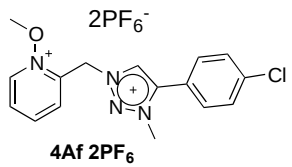

145.61
145.10
141.47
141.31
133.25
131.32
130.39
130.04
129.87
126.68
125.88
117.91
114.20
69.57
50.34
39.97 DMSO
39.80 DMSO
39.72
39.63 DMSO
39.47 DMSO
39.30 DMSO
39.13 DMSO
38.97 DMSO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2PF6-
CF3

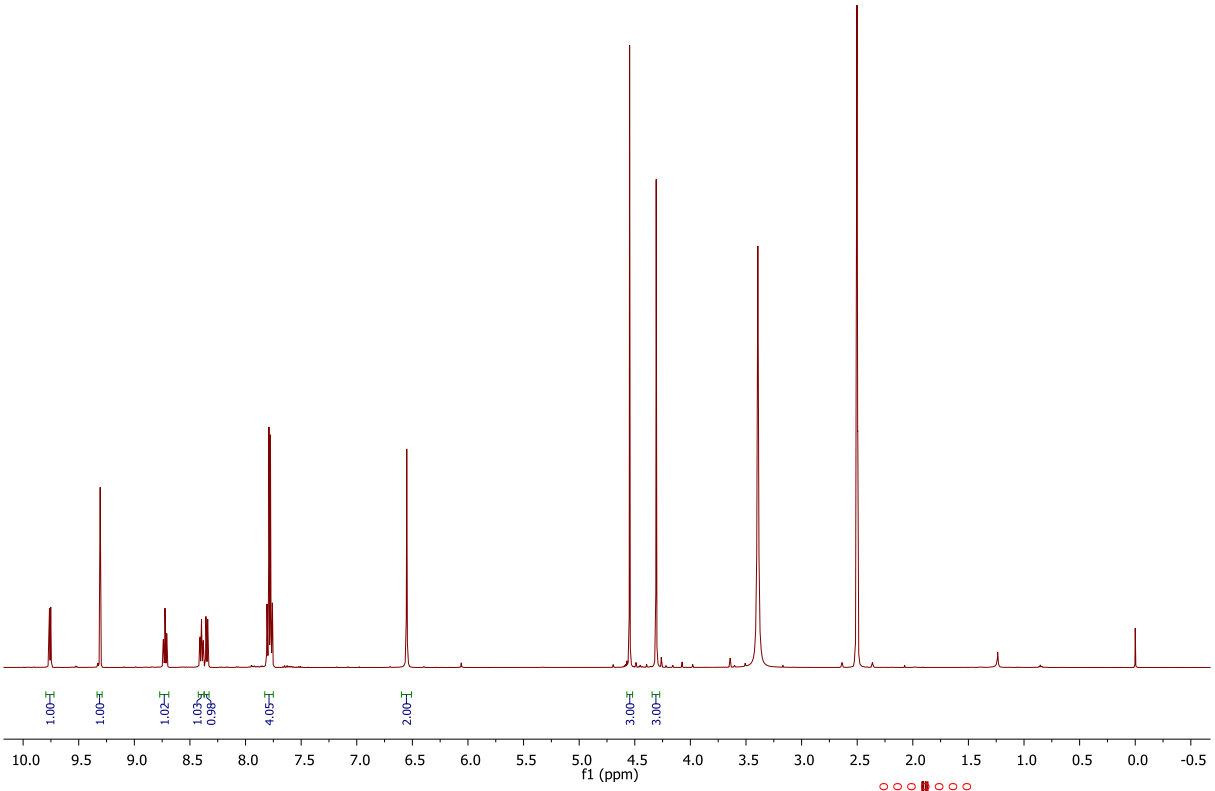
4Ae 2PF$_6$

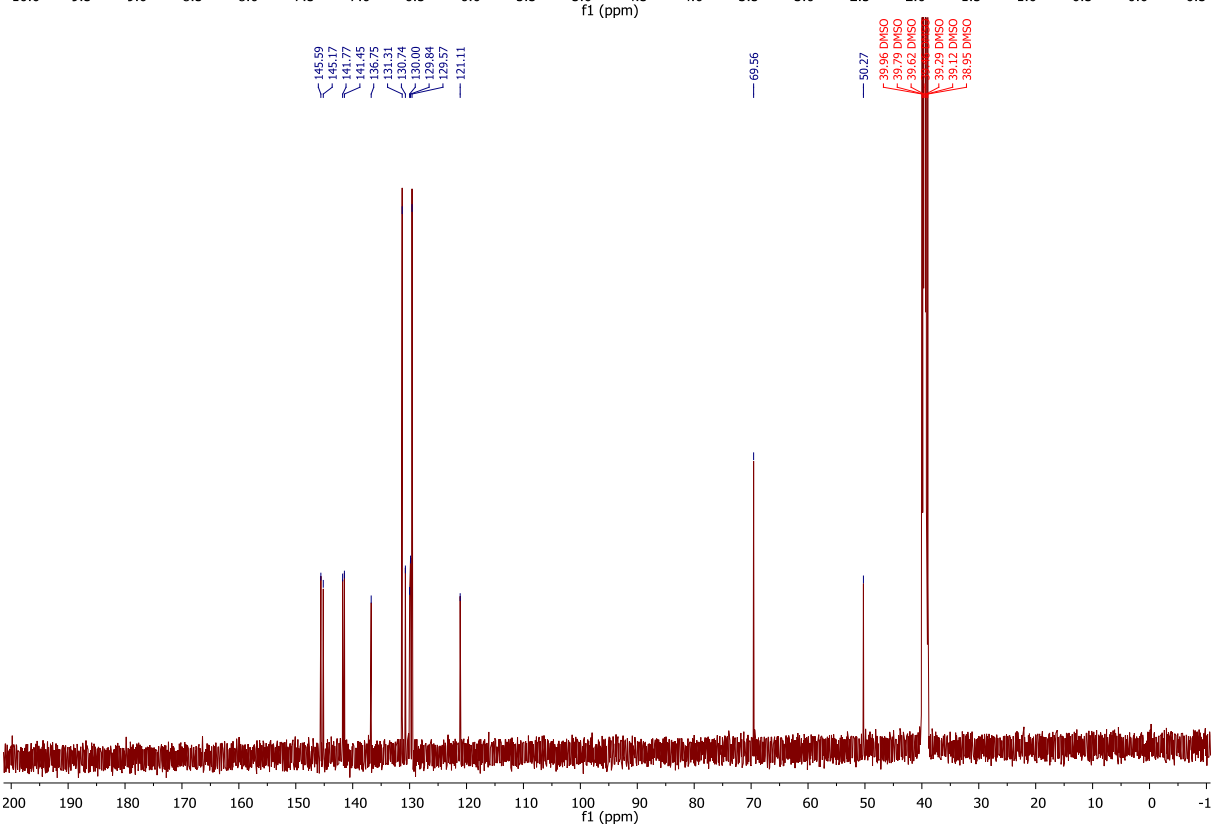

1.00
1.01
1.03
0.99
0.93
1.89
1.86
1.87
2.95
2.95
f1 (ppm)

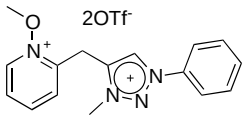

145.62
145.19
141.47
133.33
131.25
130.58
130.53
130.02
129.82
129.18
126.38
126.35
126.32
126.29
124.74
69.59
50.33
40.06 DMSO
39.97 DMSO
39.89 DMSO
39.72 DMSO
39.63 DMSO
39.56 DMSO
39.47 DMSO
39.39 DMSO
39.30 DMSO
39.13 DMSO
38.97 DMSO
35.73
f1 (ppm)


2PF6-
O
N+
N
N
N
Cl

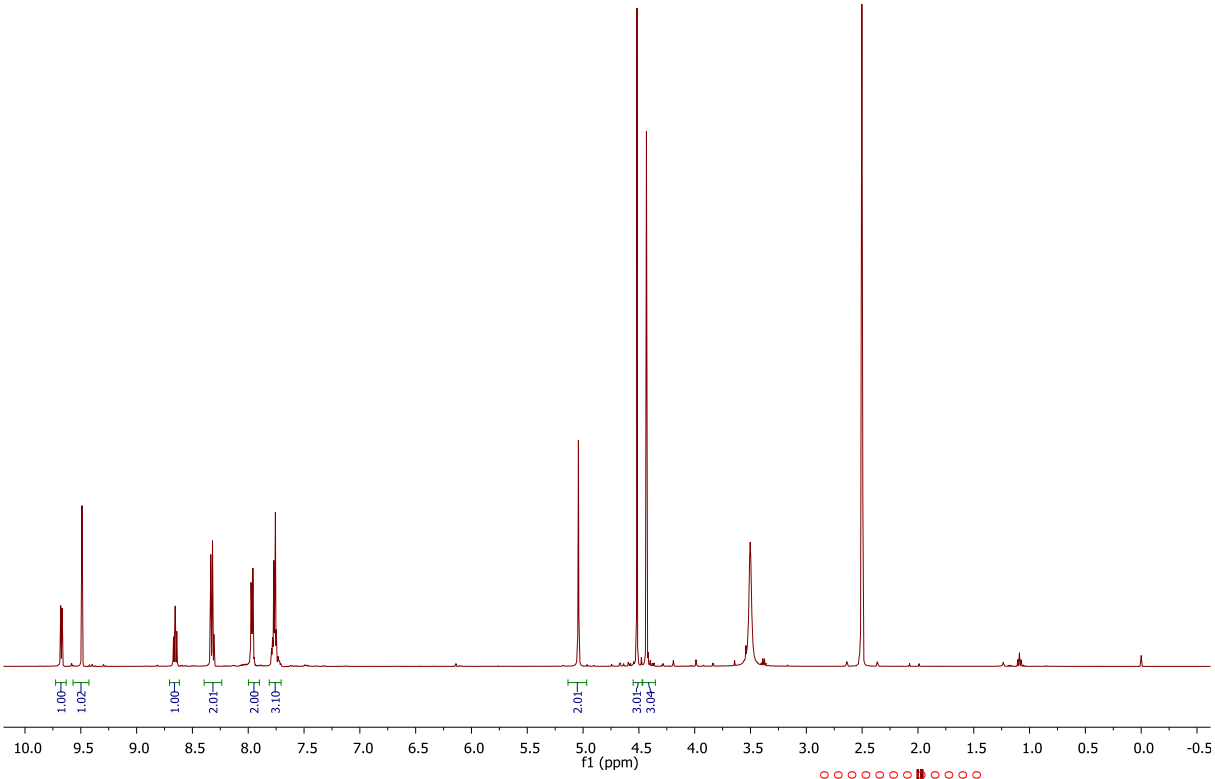
4Af 2PF$_6$

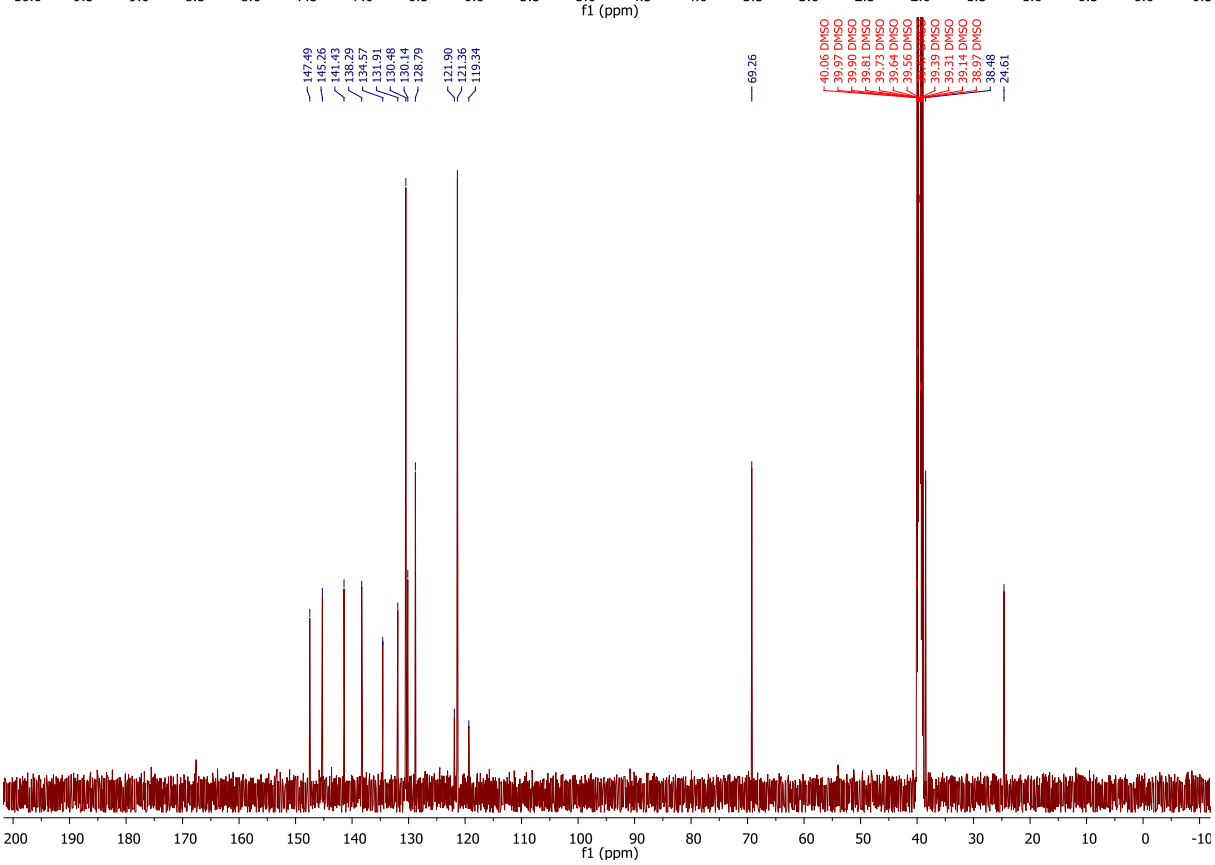

1.00
1.00
1.02
1.03
0.98
4.05
2.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

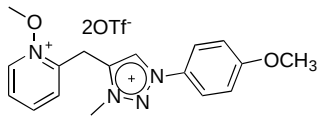

145.59
145.17
141.77
141.45
136.75
131.31
130.74
130.00
129.84
129.57
121.11
69.56
50.27
39.96 DMSO
39.79 DMSO
39.62 DMSO
39.29 DMSO
39.12 DMSO
38.95 DMSO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


2OTf-

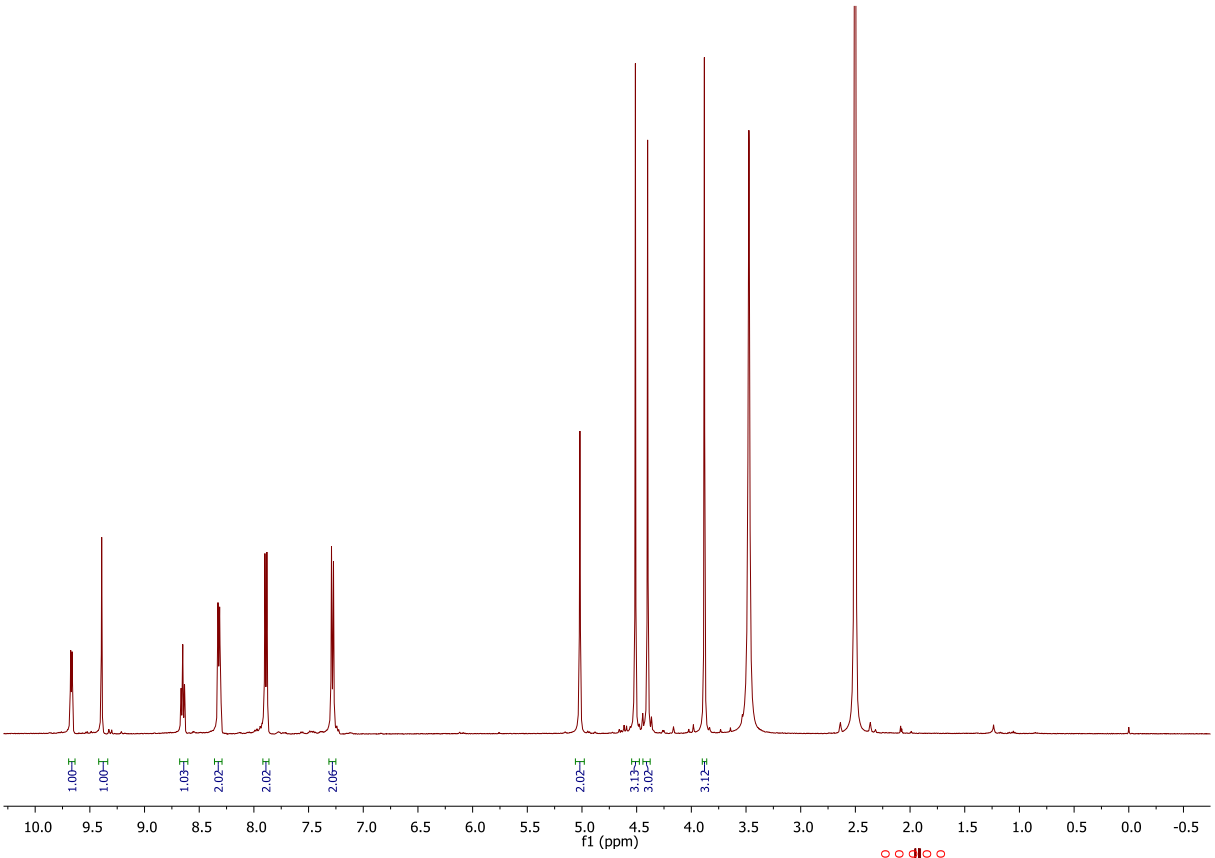
4Ba 2OTf

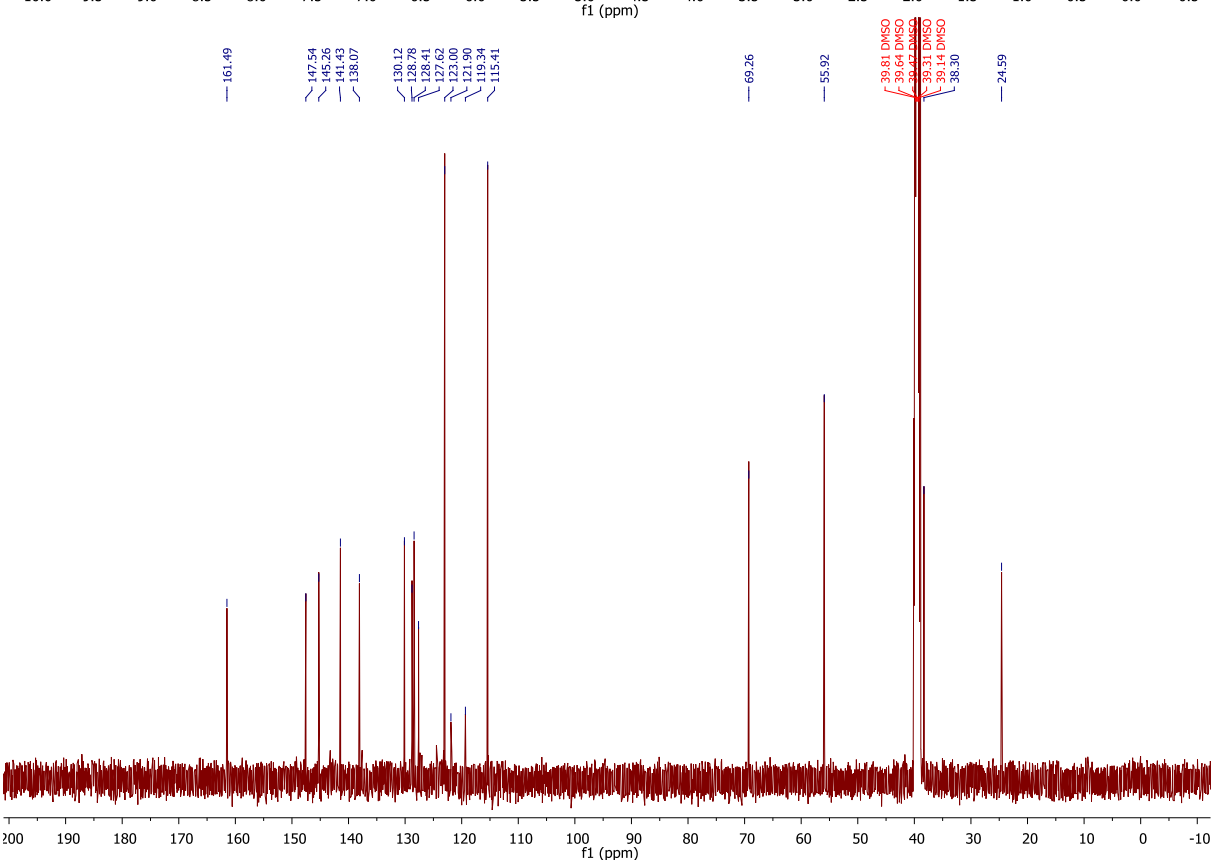

1.00
1.02
1.00
2.01
2.00
3.10
2.01
3.01
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

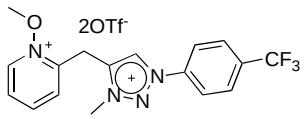

147.49
145.26
141.43
138.29
134.57
131.91
130.48
130.14
128.79
121.90
121.36
119.34
69.26
40.06 DMSO
39.97 DMSO
39.90 DMSO
39.81 DMSO
39.73 DMSO
39.64 DMSO
39.56 DMSO
39.39 DMSO
39.31 DMSO
39.14 DMSO
38.97 DMSO
38.48
24.61
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


2OTf-
OCH3

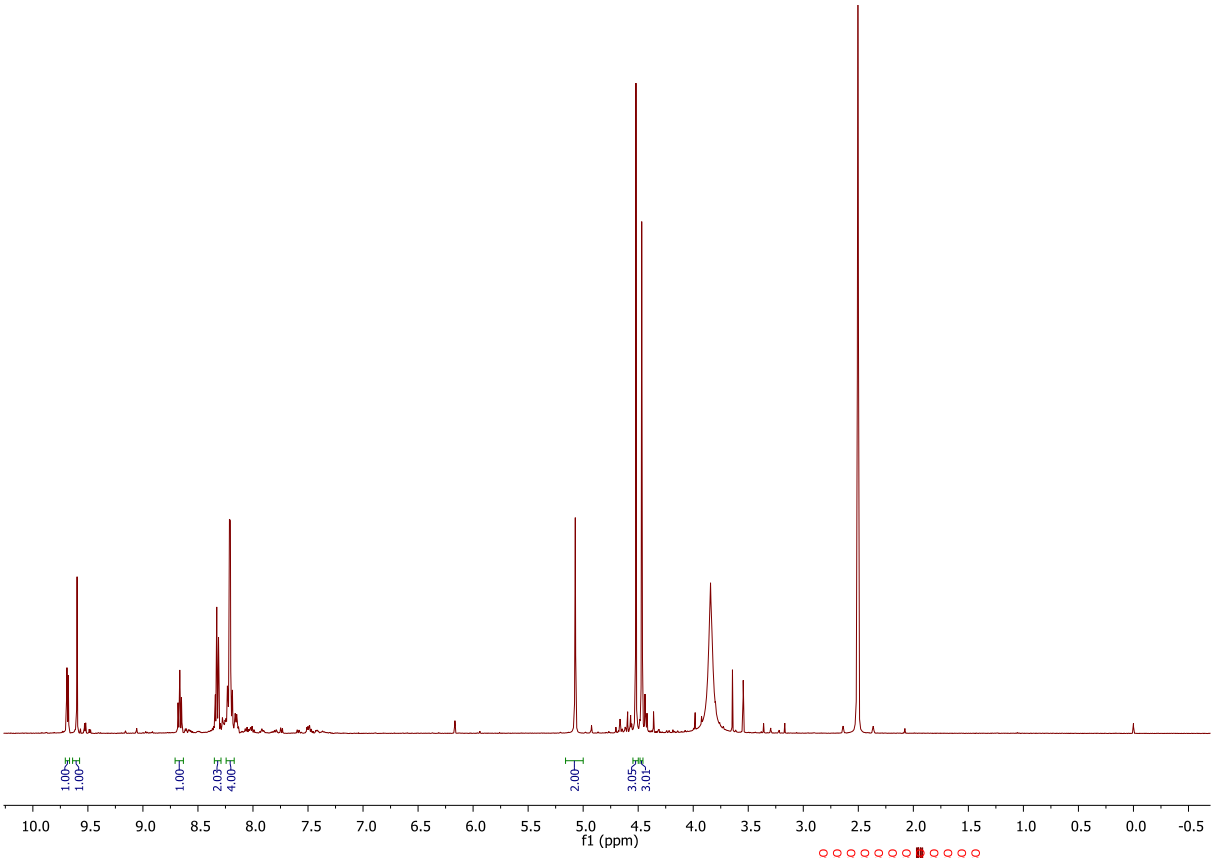
4Bc 2OTf

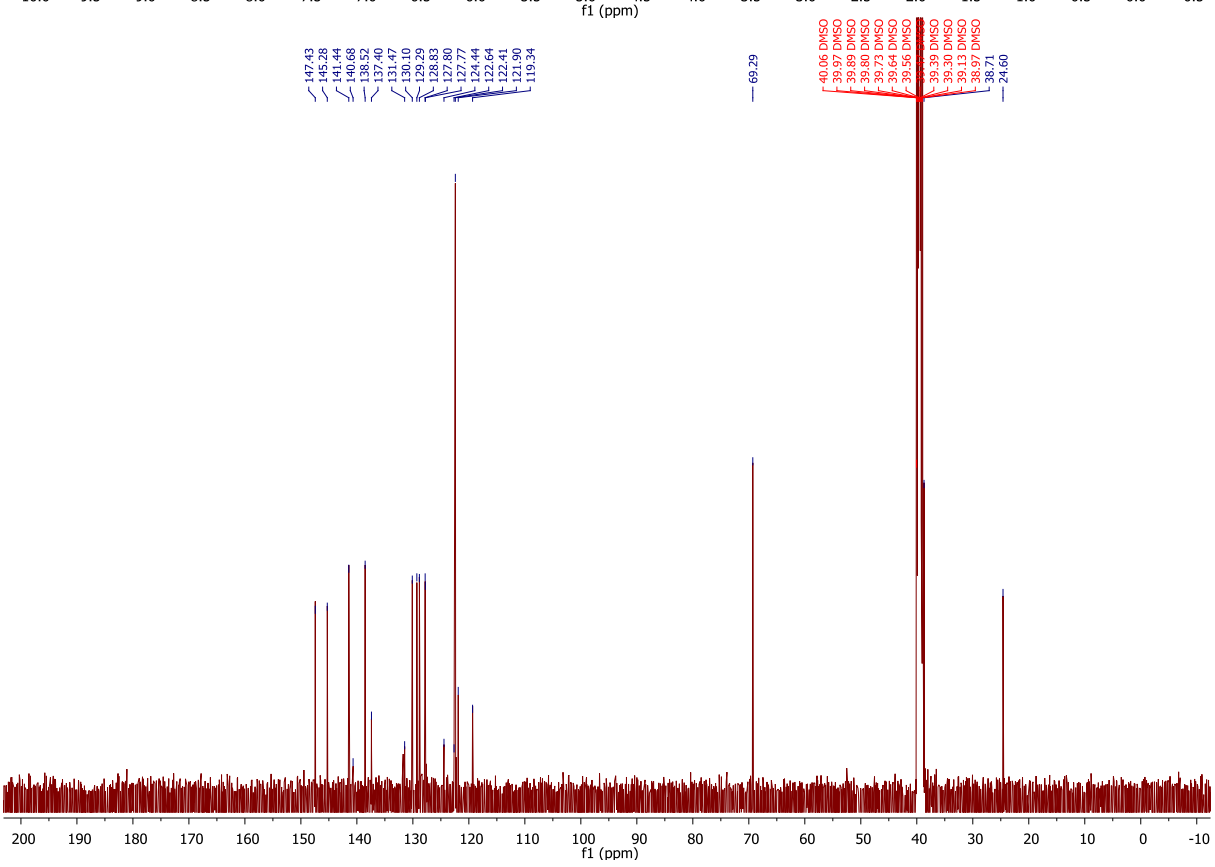

1.00
1.00
1.03
2.02
2.02
2.06
2.02
3.13
3.02
3.12
f1 (ppm)


161.49
147.54
145.26
141.43
138.07
130.12
128.78
128.41
127.62
123.00
121.90
119.34
115.41
69.26
55.92
39.81 DMSO
39.64 DMSO
39.47 DMSO
39.31 DMSO
39.14 DMSO
38.30
24.59
f1 (ppm)


2OTf-
CF3

4Be 2OTf


1.00
1.00
1.00
2.03
4.00
2.00
3.05
3.01
f1 (ppm)


147.43
145.28
141.44
140.68
138.52
137.40
131.47
130.10
129.29
128.83
127.80
127.77
124.44
122.64
122.41
121.90
119.34
69.29
40.06 DMSO
39.97 DMSO
39.89 DMSO
39.80 DMSO
39.73 DMSO
39.64 DMSO
39.56 DMSO
39.39 DMSO
39.30 DMSO
39.13 DMSO
38.97 DMSO
38.71
24.60
f1 (ppm)